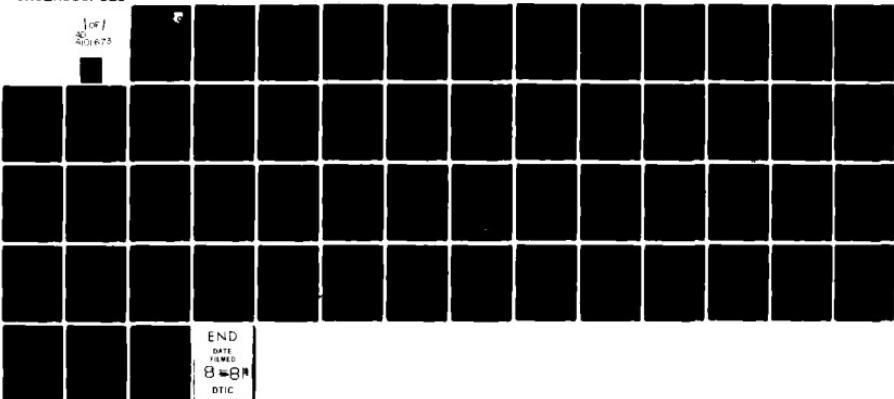


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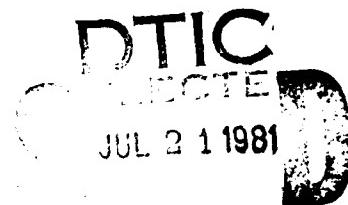


CHROMATOGRAPHIC SEPARATION OF CONVENTIONAL AND
EXPERIMENTAL FUELS

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Radian Corporation
P. O. Box 9948
Austin, Texas 78766

October 1980



TECHNICAL REPORT AFWAL-TR-80-2098
FINAL REPORT FOR PERIOD SEPTEMBER 1979 - JUNE 1980

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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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graphic method, using spherical particulate silica gel column packing and isobutane as the mobile phase. The fuel samples are fractionated by passing them through the column and collecting the eluting fractions at regular intervals. The volatile isobutane carrier is evaporated from the fractions and the residues are analyzed by techniques such as gas chromatography. Because the isobutane vaporizes quantitatively at low temperatures, the fractions are obtained free of interfering solvent. In this respect, the technique is novel and unprecedented.

Results of the analyses show that the method provides good separation of aliphatic and aromatic hydrocarbons, and partial resolution of aliphatic and olefinic hydrocarbons. Resolution may be improved substantially by optimizing the column temperature and by using low-boiling mobile phases of varying polarity.

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FOREWORD

This report describes work performed by Radian Corporation under U. S. Air Force Contract F33615-79-C-2083, to develop an improved technique for the analysis and characterization of aviation turbine fuels.

The work was performed under the technical direction of Mr. Karl J. Bombaugh as Principal Investigator, with support provided by Mr. Donald H. Rodgers and Mr. John C. Beltz.

This contractual effort was funded under Project 2303 (Chemistry), Task 2303S1 (Fuels Chemistry), Work Unit 2303S103, and administered by the Fuels Branch (AFWAL/POSF), Fuels and Lubrication Division, Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. Dr. Ronald D. Butler was the Air Force project scientist.

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SECTION I

INTRODUCTION

This report describes work done by Radian Corporation to develop a chromatographic method for the separation of aircraft fuels into the various classes of hydrocarbons of which they are composed.

The report further describes the results of the application of the method to the separation and analysis of six aircraft fuels, both conventional and experimental, supplied by the U. S. Air Force.

The physical and chemical behavior and critical performance parameters of fuels refined from natural sources are determined by the relative proportions of the various classes of hydrocarbons which make up the fuels. Because of the extreme chemical complexity of most fuels, existing methods for their analysis and characterization are not completely satisfactory. The purpose of this investigation was to develop a chromatographic procedure, using a non-interfering mobile phase, which could be used to separate the fuels of interest into several distinct compound classes. This preliminary separation would then facilitate the subsequent analysis of the fractions by more conventional techniques such as gas chromatography.

The method employed here consists of separating the fuels on a semi-preparative column packed with activated spherical particulate silica gel. The unique feature of the procedure is the use of isobutane as the mobile phase: because it has a low boiling point, the isobutane can be easily separated by evaporation from the collected fractions, thereby eliminating solvent interference problems. There is no precedent in the scientific literature for this approach.

The eluted fractions were analyzed by gas chromatographic techniques to determine the separation efficiency of the silica gel column. Calibration of both the separation column and the gas chromatographic analytical columns was achieved by the use of known model compounds, which were chosen as representative of the classes of compounds normally found in the fuels.

SECTION II

EXPERIMENTAL

A. Materials and Equipment

The following instruments, equipment, and reagents were used in this investigation:

Liquid chromatographic column: silica gel (Spherosil XOA-400), 40-100 μ particle size, was packed by the dry/tap fill method into stainless steel tubing 10 mm ID x 600 mm long. The columns were conditioned overnight at 150°C, with a flow of dry nitrogen. A smaller particle size silica gel, Lichrosorb 60, having a mean particle diameter of 30 μ , was also used to pack four 10 x 600 mm columns which were then connected in series.

Isobutane, instrument grade: liquefied isobutane, at a tank pressure of 2.1 bar (20°C) was purchased in cylinders from Phillips Petroleum Company.

Sample introduction valve: a Valco ten-port valve was used for sample injection.

Gas chromatograph: Tracor Model 560 with 3% OV-101 and 10% 1,2,3-tris(2-cyanoethoxy)propane columns.

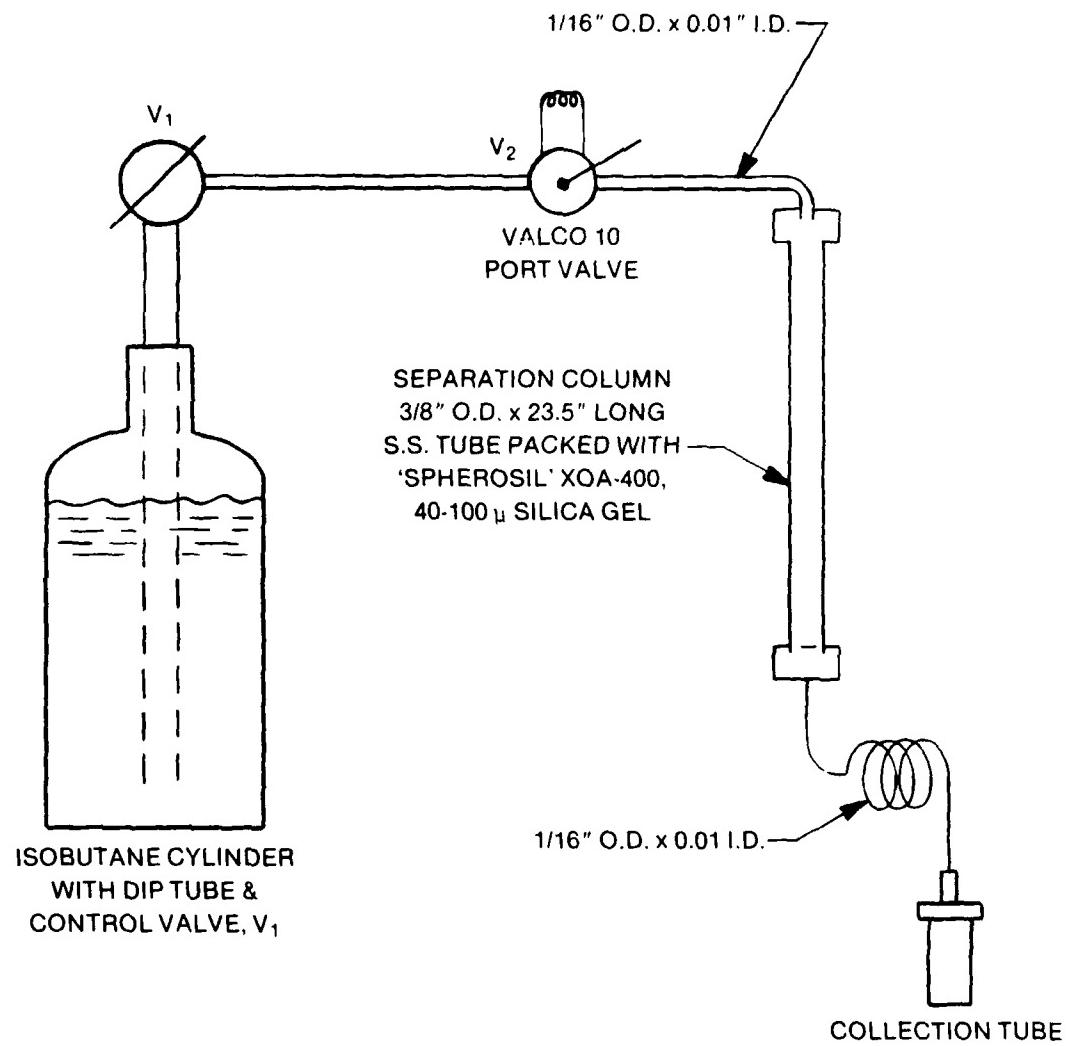
Infrared spectrophotometer: Perkin-Elmer Model 283.

Ultraviolet/visible spectrophotometer: Varian Model 219.

B. Apparatus Configuration

The chromatographic separation system was assembled as shown in Figure 1. The isobutane mobile phase was delivered through the column under its own intrinsic vapor pressure of about 2.1 bar, or at higher pressures with nitrogen pressurization. The flow rate was controlled by the use of metal capillary tubing (0.01 in ID) connected to the column outlet. The flow rate varied slightly over brief periods, but averaged about 2.5 mL/min, as measured by collection of the effluent in a chilled graduated cylinder.

The isobutane cylinder was fitted with a dip tube that passed to the bottom of the cylinder. This enabled the collection of liquid rather than gaseous isobutane. Fuel samples and calibration standards were introduced



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FIGURE 1 DIAGRAM OF SEPARATION APPARATUS

onto the column by means of the Valco valve, which was fitted with a sample loop of the desired sample volume.

C. Separation Procedure

In practice, the sample or a standard mixture was introduced onto the separation column via the ten-port valve. The effluent isobutane was then collected at regular intervals in separate chilled containers. The collected fractions were warmed to room temperature and the isobutane carrier allowed to evaporate. The residues were dissolved in carbon disulfide or other appropriate solvents for gas chromatographic, infrared, or ultraviolet measurement. The data obtained from the collected fractions were compared with similar data obtained for the initial neat sample mixture to determine the degree of fractionation.

D. System Calibration

In order to determine the separation efficiency of the system, various calibration mixtures of known compounds were injected onto the column and collected in the effluent. A mixture of hexane, benzene, and naphthalene was chosen as representative of aliphatic and aromatic compounds. Subsequently, mixtures of hexane, cyclohexane, and isopentane were chromatographed and collected. The mixtures were chosen as representative of linear, cyclic, and branched aliphatic hydrocarbons.

Finally, n-octane, 1-octene, *trans*-2-octene, and 2,2,4-trimethylpentane were tested for retention volume in the system. These compounds were chosen as representative of normal, branched, and olefinic hydrocarbons.

In addition to the separation system, mixtures of known hydrocarbons were used as gas chromatography standards to provide retention time data for the identification of various compounds in the liquid chromatographic fractions.

E. Sample Fractionation and Identification

Following calibration of the system, six samples of authentic jet fuels were analyzed by the method. These samples were supplied to Radian by the Air Force project scientist. Separation and fraction collection were carried out as described above. In addition to the isobutane elution, however, a final elution with methylene chloride was carried out on each sample. This final "column wash" was included to remove completely any strongly adsorbed sample components from the column. Four separate fractions were collected, including the final methylene chloride wash. The collected fractions were then analyzed by gas chromatography, and the remaining residues were submitted to the Air Force project scientist for further analysis.

SECTION III

RESULTS AND DISCUSSION

A. System Calibration

The activated separation column was first tested for separation efficiency using standard mixtures of hexane, benzene, and naphthalene as described in Section II. Fractions of the eluate were collected at five-minute intervals and analyzed by gas chromatography for the presence of the three compounds. The results showed that the hexane eluted primarily in the 10-15 minute fraction, benzene in the 20-30 minute fraction, and naphthalene in a broad band from 35 to 115 minutes, with 75% eluting in 40-60 minutes.

The experiment was repeated several times using only hexane and benzene mixtures, resulting in an estimated separation factor >7 for these two compounds. (Separation factor is the ratio of the uncorrected retention times.)

The system was next tested for the separation of normal, branched, and cyclic aliphatic hydrocarbons, using hexane, cyclohexane, and isopentane. Fractions were collected at one-minute intervals and analyzed by gas chromatography. The results showed that these three compounds were poorly separated, and were entirely eluted in the fractions collected between 11 and 15 minutes. Elution profiles of these compounds are shown in Figure 2.

In an attempt to increase resolution, a series of four 600-mm Lichrosorb 60 packed columns were connected in series with the Spherosil column, giving a fivefold increase in column length. To provide adequate carrier flow, the isobutane cylinder was pressurized to 5.4 bar with nitrogen. A mixture of the three test compounds was injected and fractions were collected at five-minute intervals. Analysis of the fractions showed that isopentane eluted first between 100 and 120 minutes, and was almost completely resolved from the hexane and cyclohexane, which were poorly resolved. Repetition of the experiment confirmed these results and suggested that hexane eluted slightly before cyclohexane, but with considerable peak overlap. The elution profiles of the three compounds are shown in Figure 3.

A further attempt to improve the resolution of these compounds was made by lowering the temperature of the three-meter column to 0°C. This was accomplished by immersing the columns in an ice bath. Considerable experimental difficulty was encountered, making the results somewhat ambiguous. However, the results which were obtained appeared to indicate poorer, rather

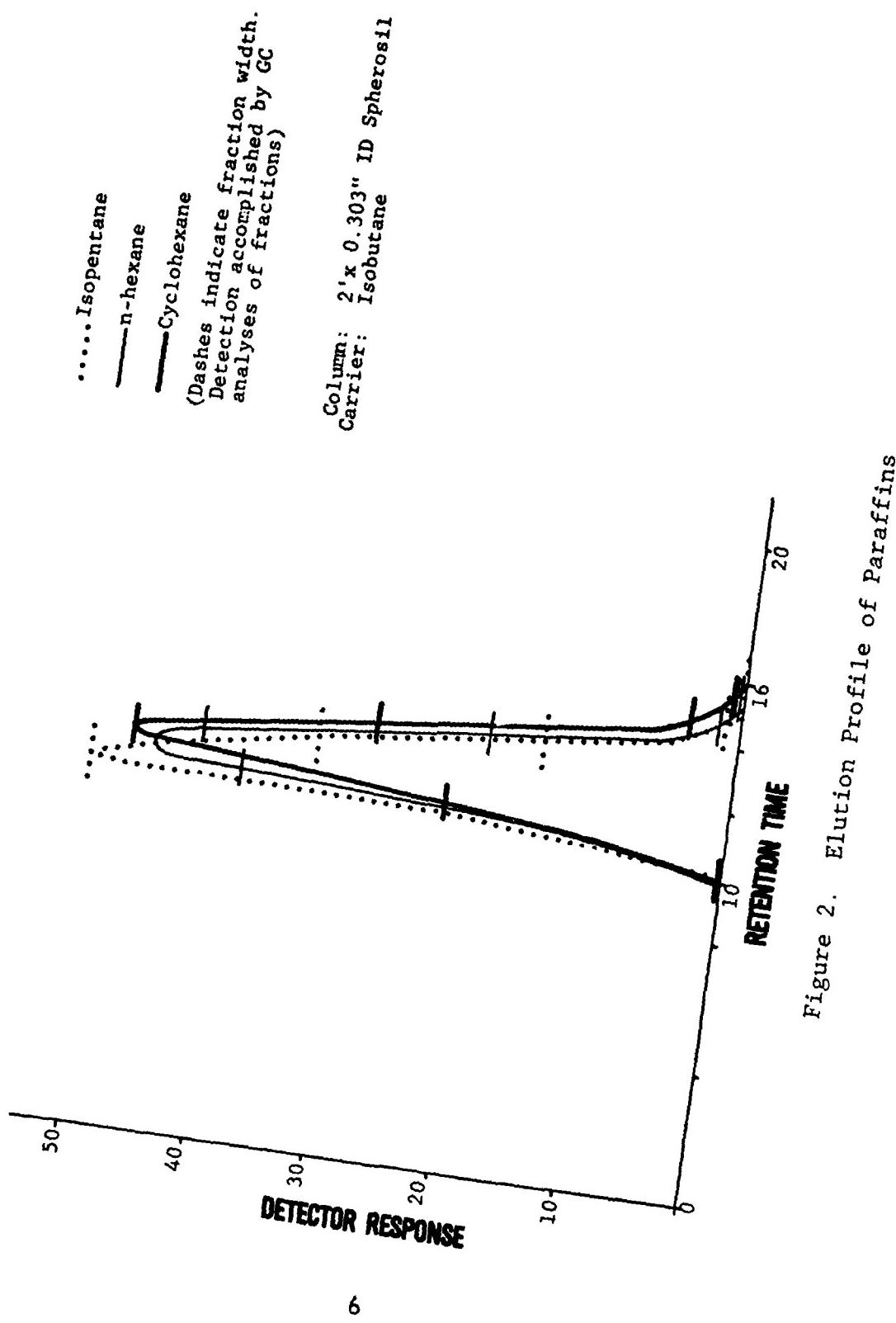


Figure 2. Elution Profile of Paraffins

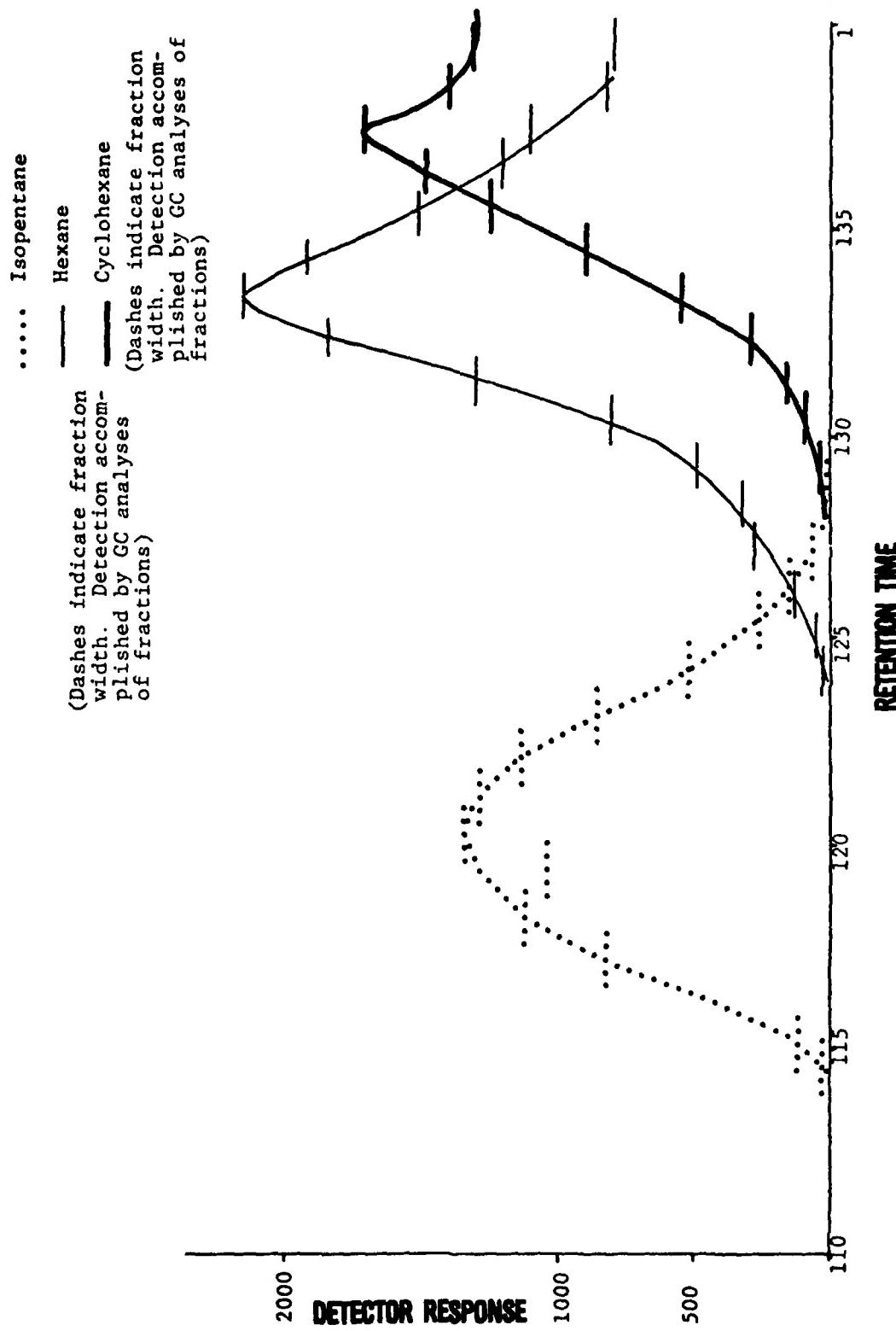


Figure 3. Elution Profiles of Paraffins

than better, resolution of the hexane and cyclohexane. Initially, the data seemed to indicate very long retention times (longer than four hours) with cooling. Repetition of the experiment, however, showed that the components were in fact eluted in the first 100 mL of effluent, or essentially in the solvent front. We are unable to explain these results. No further experiments were performed with column temperature variation.

A final series of calibration tests were made in order to determine the resolution efficiency of the system for saturated and olefinic compounds. n-Octane, 2,2,4-trimethylpentane, 1-octene, and *trans*-2-octene were chromatographed and the fractions analyzed. It was found that the two saturated octanes coeluted in the 10-14 minute fraction (the same as hexane), while the two octene compounds coeluted in 14-16 minutes. Elution profiles of these compounds are shown in Figures 4 and 5.

The gas chromatographic systems were calibrated with the same standards used for the liquid column measurements. In addition, calibration mixtures containing various alkylbenzenes, and also C₁₁ to C₂₀ hydrocarbons, were chromatographed to obtain retention time data for the identification of column fraction components.

B. Analysis of Fuel Samples

Six jet fuel samples were received from the Air Force for study. The samples as received were examined by infrared and ultraviolet spectrophotometry, and by gas chromatography using both selective and non-selective columns. These preliminary measurements were made to determine the approximate composition of the samples with regard to their aromatic and aliphatic character, and to aid in the later interpretation of the column fraction data. The infrared spectra are shown in Figures 6-11. Sample 3936 was shown to be the most aromatic, and sample 3939 the most paraffinic.

The samples were then subjected to liquid chromatographic separation by the techniques described previously. Four fractions were collected for each sample, and each of the four fractions was analyzed by gas chromatography.

Other intermediate fractions were also collected for most of the samples; however, only those fractions containing hydrocarbon residues (as evidenced by gas chromatographic analysis) were studied and included in this report.

The gas chromatograms obtained for samples 3934 through 3939, and for the respective fractions, are shown in the accompanying figures. The first chromatogram in each set was obtained with the neat sample. A discussion of the individual sample results follows. The assignment of component identities is based primarily on gas chromatographic retention times and their coincidence with known standards.

1. Sample 3934 (JP-4). This sample contains a large fraction of low-boiling, nonpolar substances such as paraffinic hydrocarbons, a comparable amount of higher-boiling hydrocarbons (approximately C₉ to C₁₄), and a smaller amount of strongly retained materials.

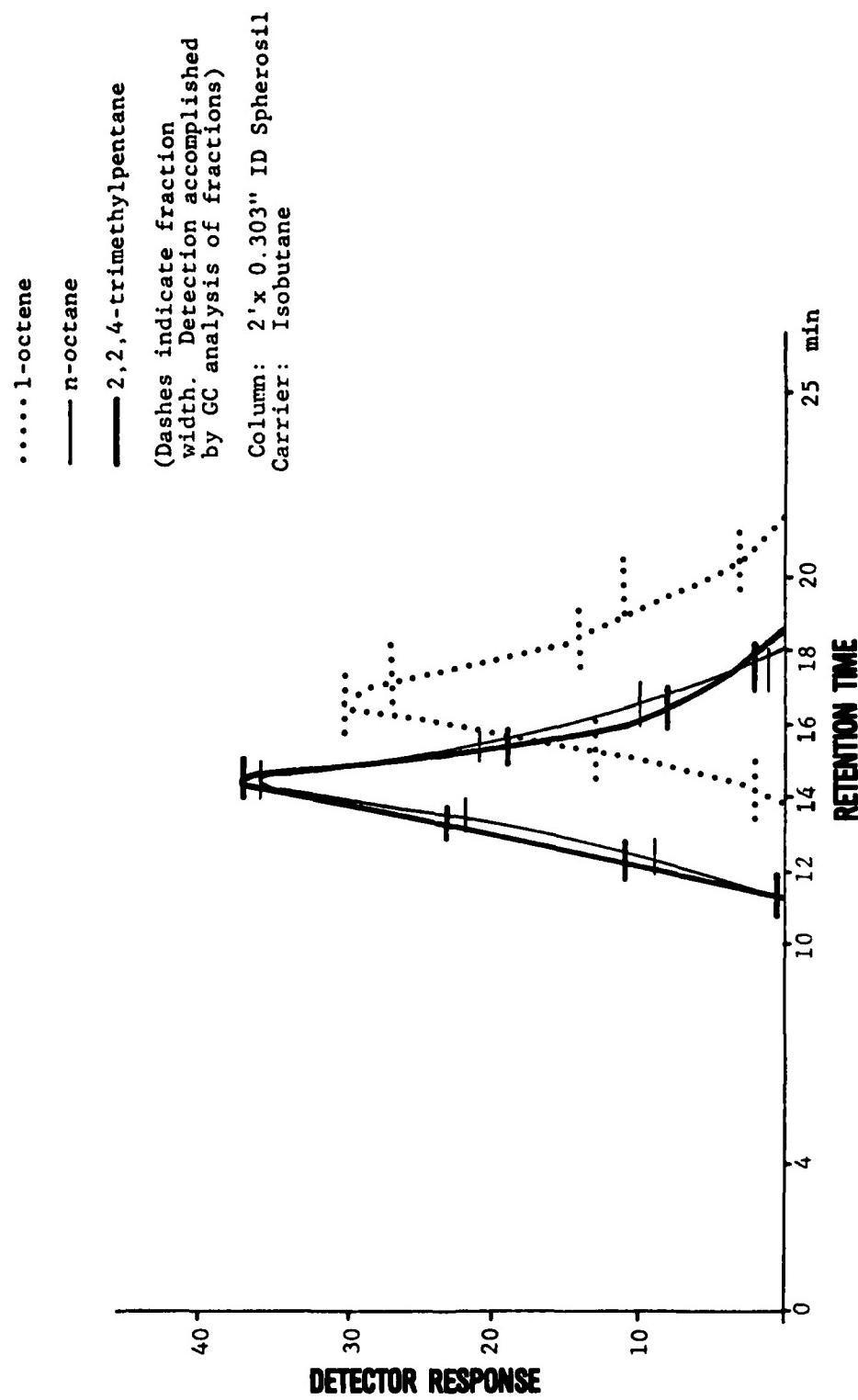


Figure 4. Elution Profile of Octanes and Octene.

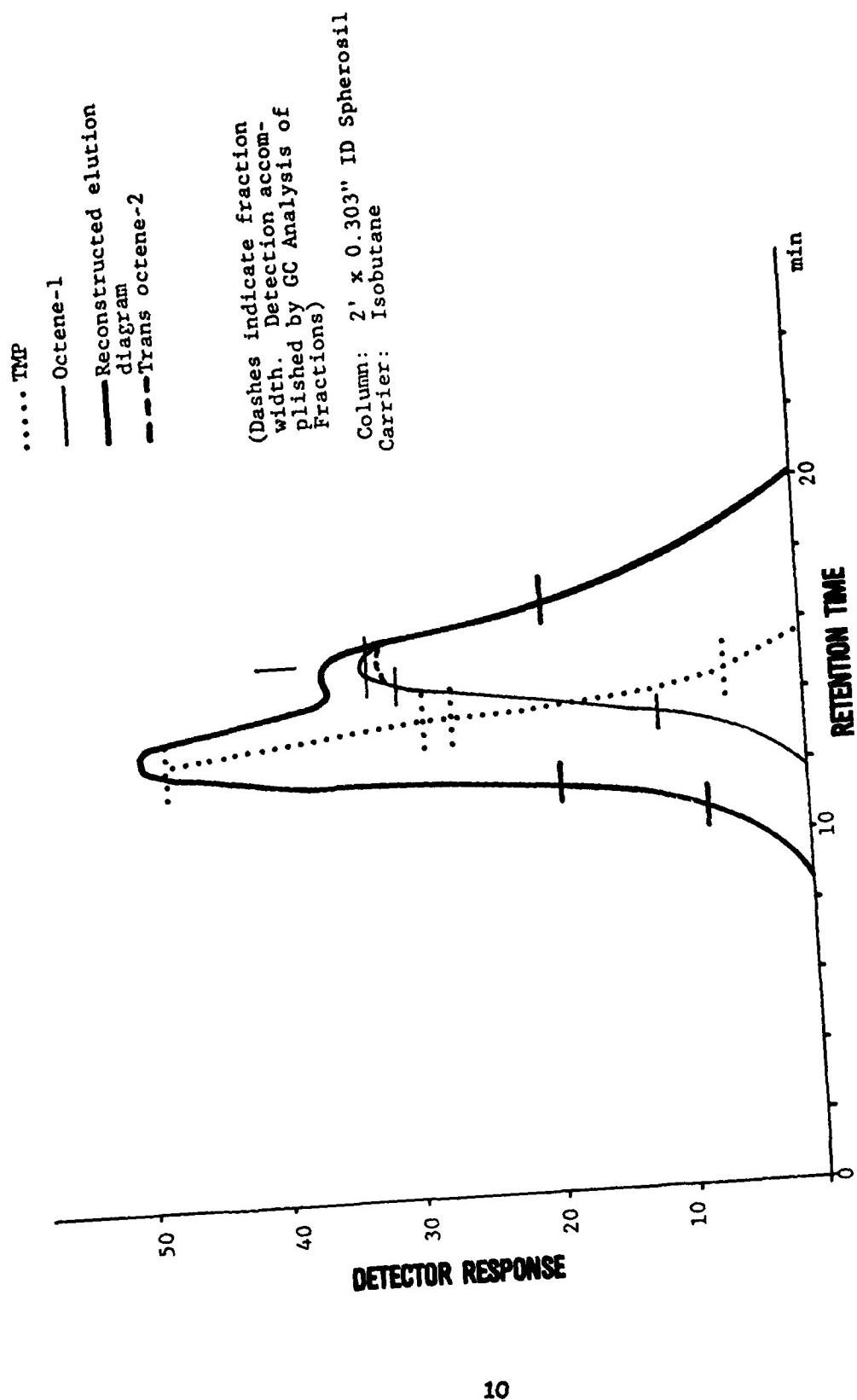


Figure 5. Elution Profile of Octene and Octane.

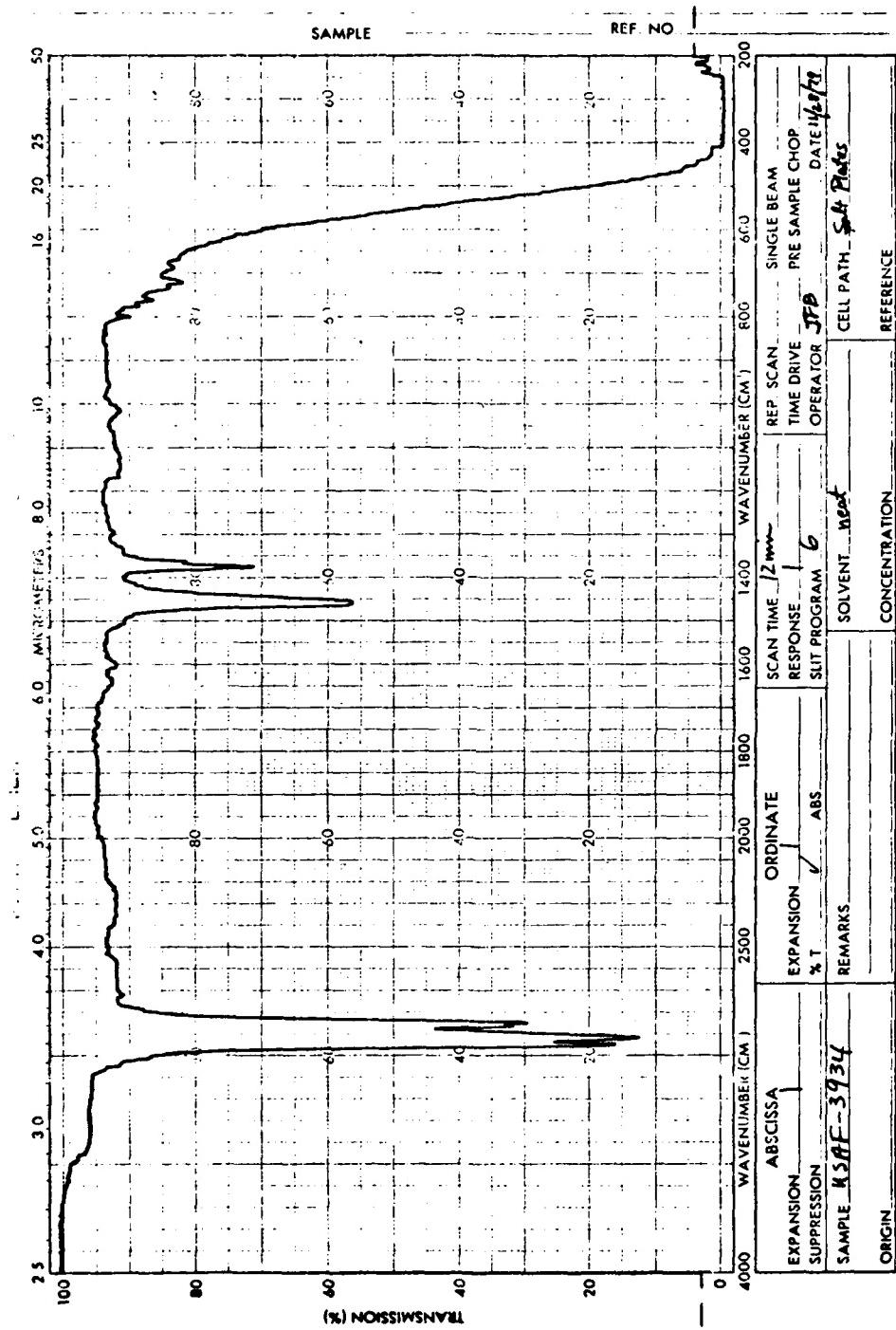


Figure 6. Infrared Spectrum of Sample 3935; JP-4 Fuel

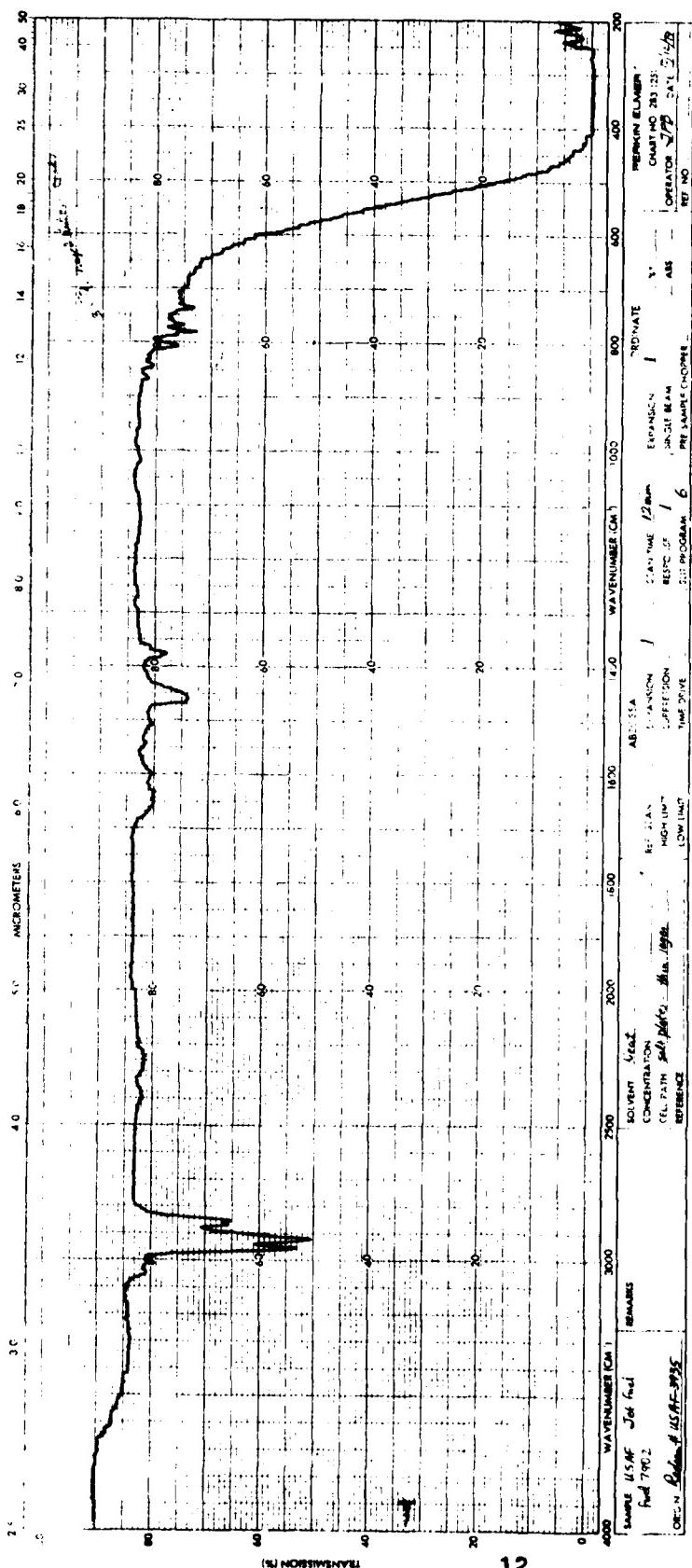


Figure 7. Infrared Spectrum of Sample 3935; JP-4A2 Fuel

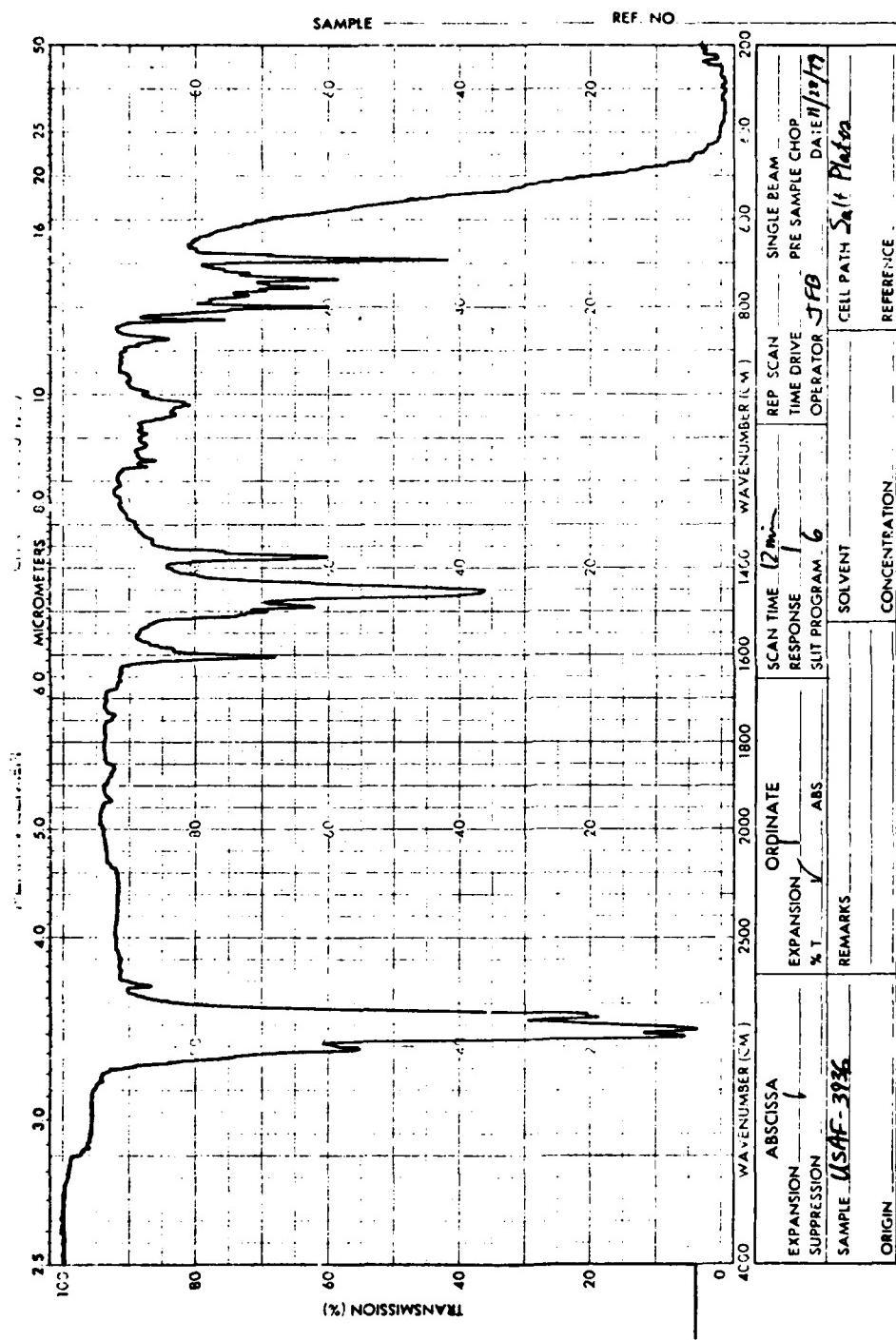


Figure 8. Infrared Spectrum of Sample 3935; JP-4X2 Fuel

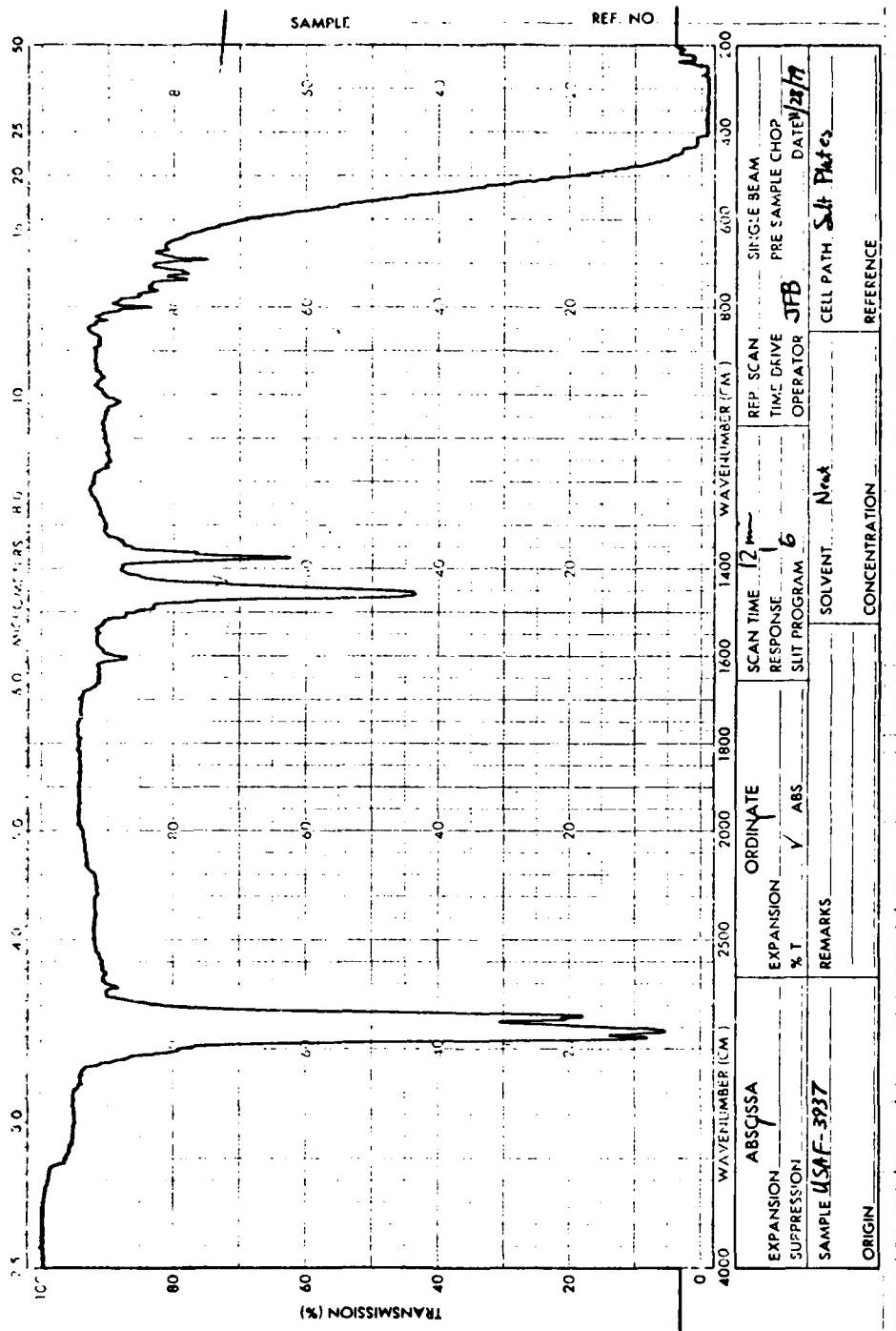


Figure 9. Infrared Spectrum of Sample 3937; JP-4X/04 Fuel

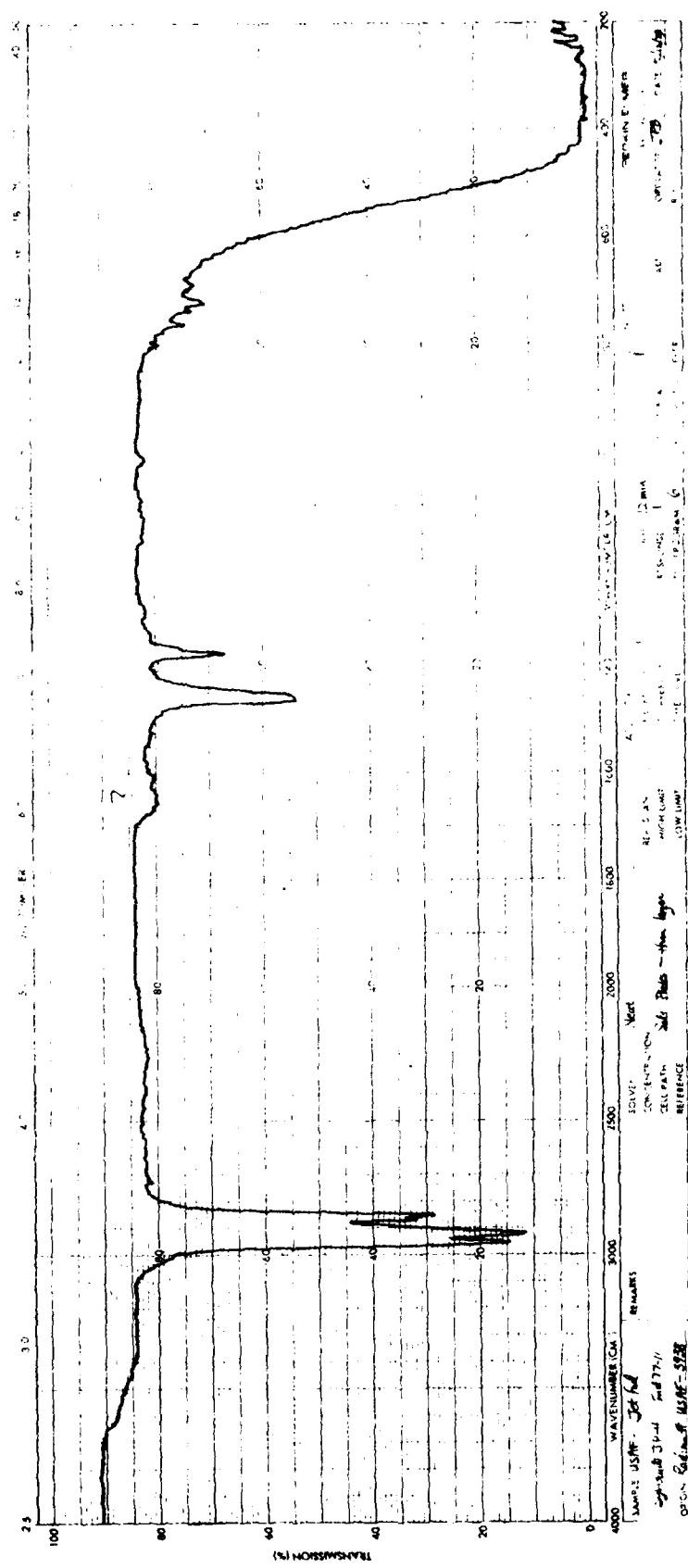


Figure 10. Infrared Spectrum of Sample 3938; Syncrude JP-4 Fuel

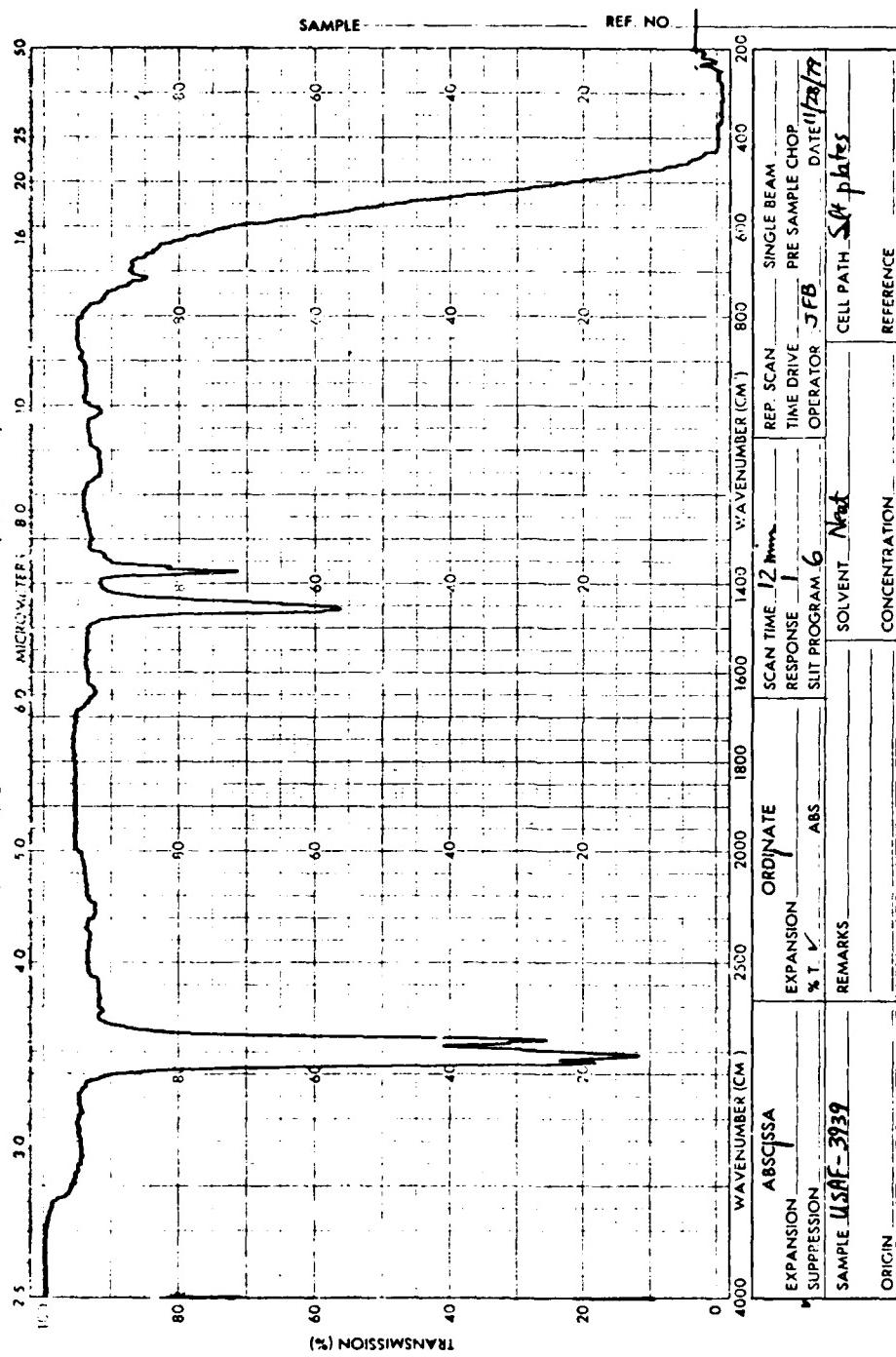


Figure 11. Infrared Spectrum of Sample 3939; JP-7 Fuel

LC fraction 1, collected from 0-10 minutes, contained both the light and intermediate paraffin. Fraction 2, 10-15 minutes, was similar to fraction 1. Fraction 3 (15-22 minutes) contained only a trace of paraffins and some light aromatic compounds. Fraction 4 showed primarily alkylaromatics, and possibly naphthalenes or other bicyclic aromatics. Other polycyclic compounds of higher molecular weight than naphthalene may also have been present; however, we did not attempt to identify these species.

The gas chromatograms of the neat sample 3934 and fractions 1-4 are shown in Figures 12-16.

2. Sample 3935 (JP-4A2). This sample contains a large amount of light hydrocarbon (C_9 to C_{14}), plus a relatively large amount of bicyclic aromatic material.

LC fraction 1 (0 to 7 minutes) contained the light and intermediate paraffins. Fraction 2 (7-14 minutes) contained the paraffins, plus some aromatics. It appeared that some column channeling occurred with this sample since both alkylaromatic and aliphatic compounds are present in fraction 2. Fraction 3 (14-19 minutes) was free of paraffins, and contained both aromatic and bicyclic compounds. Fraction 4 contained only the bicyclic compounds.

Figures 17-21 show the gas chromatograms of the neat sample 3935 and fractions 1-4.

3. Sample 3936 (JP-4X2). Sample 3936 appears to contain two groups of substances, a light paraffin fraction and an alkylaromatic fraction. The paraffin fraction was found to contain primarily C_6 hydrocarbons, with much smaller amounts of C_8 and C_9 compounds. The alkylaromatic fraction is apparently mainly C_3 alkylbenzenes. Lower hydrocarbons, such as C_2 - C_4 , were probably lost in the isobutane evaporation step; no attempt was made to detect these compounds.

LC fraction 1 (0-10 minutes) contained the C_6 and higher paraffins. Fraction 2 (10 to 25 minutes) contained a mixture of paraffins and alkylaromatics. Fraction 3 contained alkylaromatics, plus a trace of naphthalenes. Fraction 4, eluted with methylene chloride, contained traces of alkylaromatics and the more polar bicyclic compounds. Gas chromatograms of these samples are shown in Figures 22-26.

4. Sample 3937 (JP-4X/04). This sample contains a wide range of aliphatic hydrocarbons, plus some alkylaromatics. LC fraction 1 (0 to 13 minutes) contained the paraffinic compounds, consisting of the normal alkanes to C_{21} . Fraction 2 (14 to 15 minutes) contained some paraffins, from overlap of fraction 1, plus alkylaromatics. Fraction 3 (16 to 20 minutes) contained benzene, toluene, xylenes, and trimethylbenzenes. Fraction 4, the methylene chloride flush, contained both alkylaromatics and bicyclic aromatics.

The gas chromatograms for the neat sample 3937 and the four fractions are shown in Figures 27-31.

5. Sample 3938 (Syncrude JP-4). This sample was found to contain a

narrow distribution of paraffins. In addition to the light paraffins, C₆ to C₈, it contained a relatively large proportion of C₁₀ and C₁₁ compounds and only a trace of C₁₃ to C₁₈ paraffins.

LC fraction 1 (10 to 13 minutes) contained only paraffins. Fraction 2 (13 to 16 minutes) was similar to fraction 1. Fraction 3 (16 to 20 minutes) contained alkylaromatics, and fraction 4 contained aromatics plus a trace of bicyclic hydrocarbons.

Although the aromatic naphthalene separation was not as good in this run as in the previous runs, the paraffin separation was superior. This type of inconsistency is probably caused by variations in the activity of the silica gel. Such variations may be corrected by improved procedures for activation of the column and by continuous monitoring of the column effluent.

Figures 32-36 illustrate the gas chromatograms of the neat sample of the four isolated fractions.

6. Sample 3939 (JP-7). Sample 3939 showed a distinctly different distribution from the other samples. The data indicate that this sample consists of a narrow range, higher-boiling mixture of nonaromatic hydrocarbons.

LC fraction 1 (0 to 10 minutes) contained a small amount of C₁₀ to C₁₄ compounds. Fraction 2 (10 to 15 minutes) contained a large amount of material which was also C₁₀ to C₁₄ compounds. Fraction 3 (15 to 20 minutes) gave no measurable residue upon evaporation of the carrier. The methylene chloride flush, fraction 4, contained a small amount of various other compounds.

From the GC retention times of the substances in fraction 4, they appear to be bicyclic. It may be concluded, therefore, that they may be naphthalenic or naphthalene derivatives.

Figures 37-40 show the gas chromatograms for the neat sample and fractions 1, 2, and 4.

Samples of the various fractions obtained from the six fuel samples have been submitted to the Air Force project scientist for further analysis.

Operator JFB Date 4 APP.
 COLUMN No. TCEP Length 9 ft. Dia. 10%
 Coating Support Mesh.
 TEMP: Col: Init. 40 °C Final 160 °C
 Rate 5 °C/min. Det. 250 °C Inf. 200 °C
 CARRIER GAS He Rate 20 ml/min.
 Pressures: Inlet Outlet
 Hydrogen ml/min. Air ml/min.
 DETECTOR: FID ; m.a. m.v.
 Scavenger Rate ml/min.
 Sens. Rec. range mv.
 SAMPLE 3934-0 Size 0.3 u.l.
 Solvent Concn.

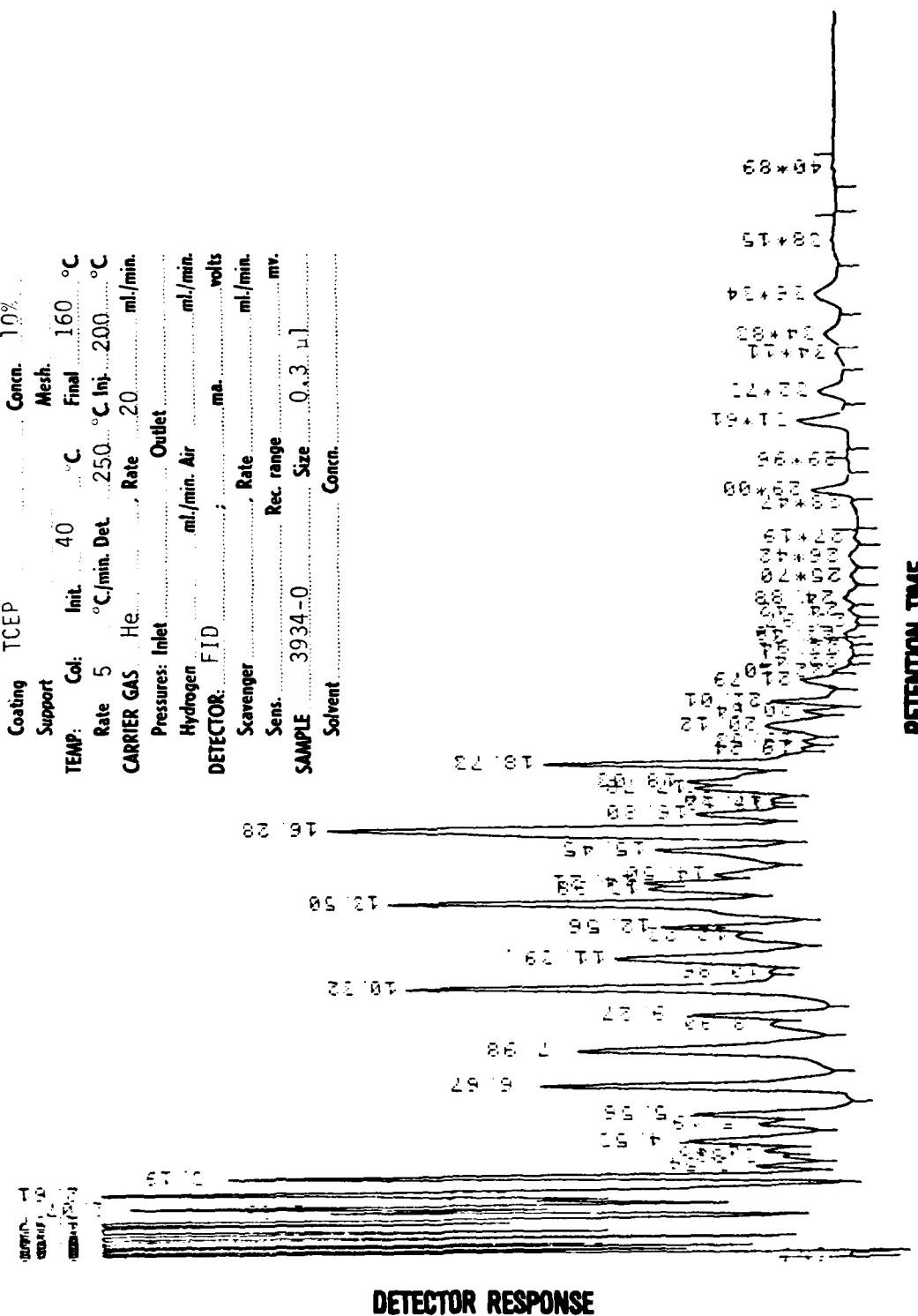


Figure 12. Gas Chromatogram of Sample 3934, Neat

Operator	JFB	Date	15 APR
COLUMN No.	TCEP	Length	9 ft.
Coating	TCEP	Dia.	10%
Support		Mesh	
TEMP:	Col: 5 °C	Init. 40 °C	Final 160 °C
Rate	°C/min. Det.	250 °C/h.	200 °C
CARRIER GAS	He	Rate	20 ml./min.
Pressures: Inlet Outlet			
Hydrogen	ml./min.	Air	ml./min.
DETECTOR:	FID	ma.	volts
Scavenger		Rate	ml./min.
Sens.		Rec. range	mv.
SAMPLE	3934-1	Size	0.2 μ
Solvent		Concn.	

DETECTOR RESPONSE

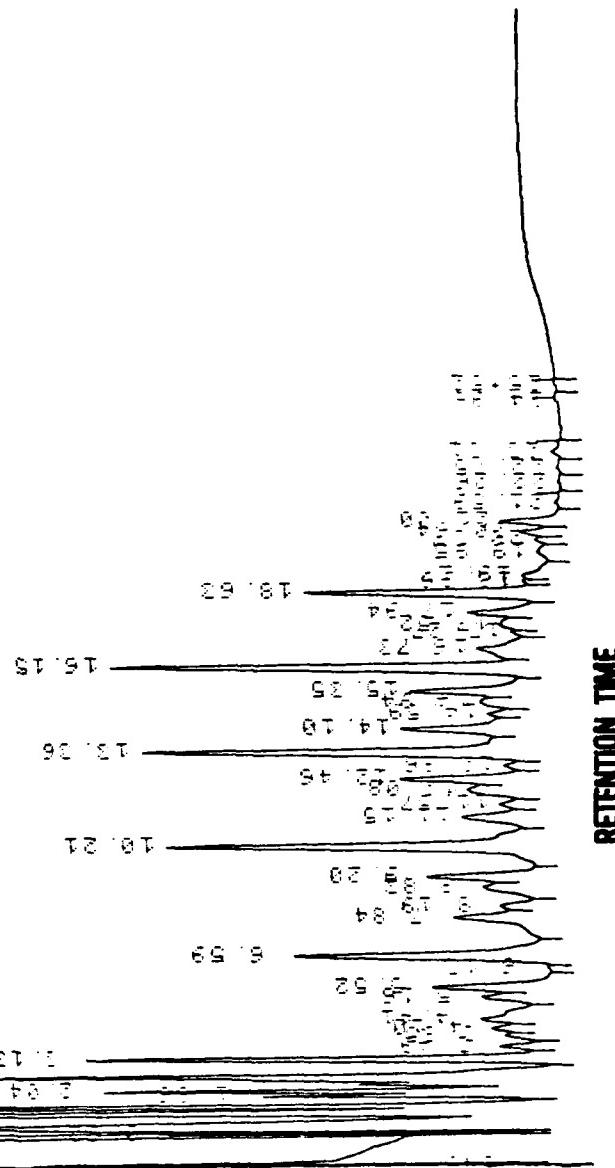


Figure 13. Gas Chromatogram of Sample 3934, LC Fraction 1

Operator	JFB	Date	15 APR
COLUMN No.	TCEP	Length	9 ft
Coating		Dia.	10 ¹⁰
Support		Mesh.	
TEMP:	Col: Init. 40 °C	Final	160 °C
	Rate 5 °C/min.	Det. 250 °C	Inj. 200 °C
CARRIER GAS	He	Rate	20 ml./min.
Pressures: Inlet		Outlet	
Hydrogen	ml./min.	Air	ml./min.
DETECTOR: FID	ma.	Rate	volts
Scavenger			ml./min.
Sens.	Rec. range	Size	mv.
SAMPLE	3934-2	0.2 μ l	
Solvent		Concn.	

Detector Response

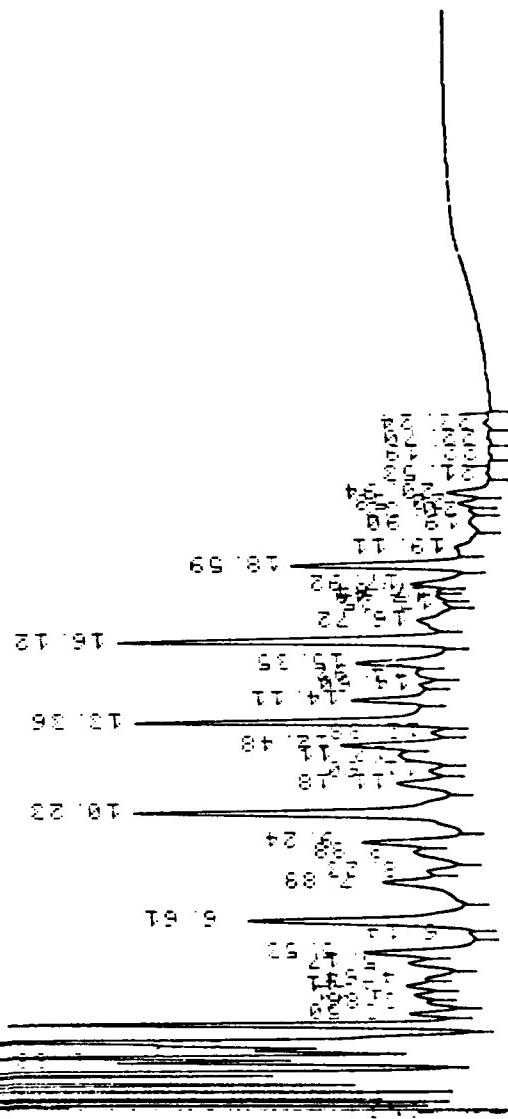


Figure 14. Gas Chromatogram of Sample 3934, LC Fraction 2

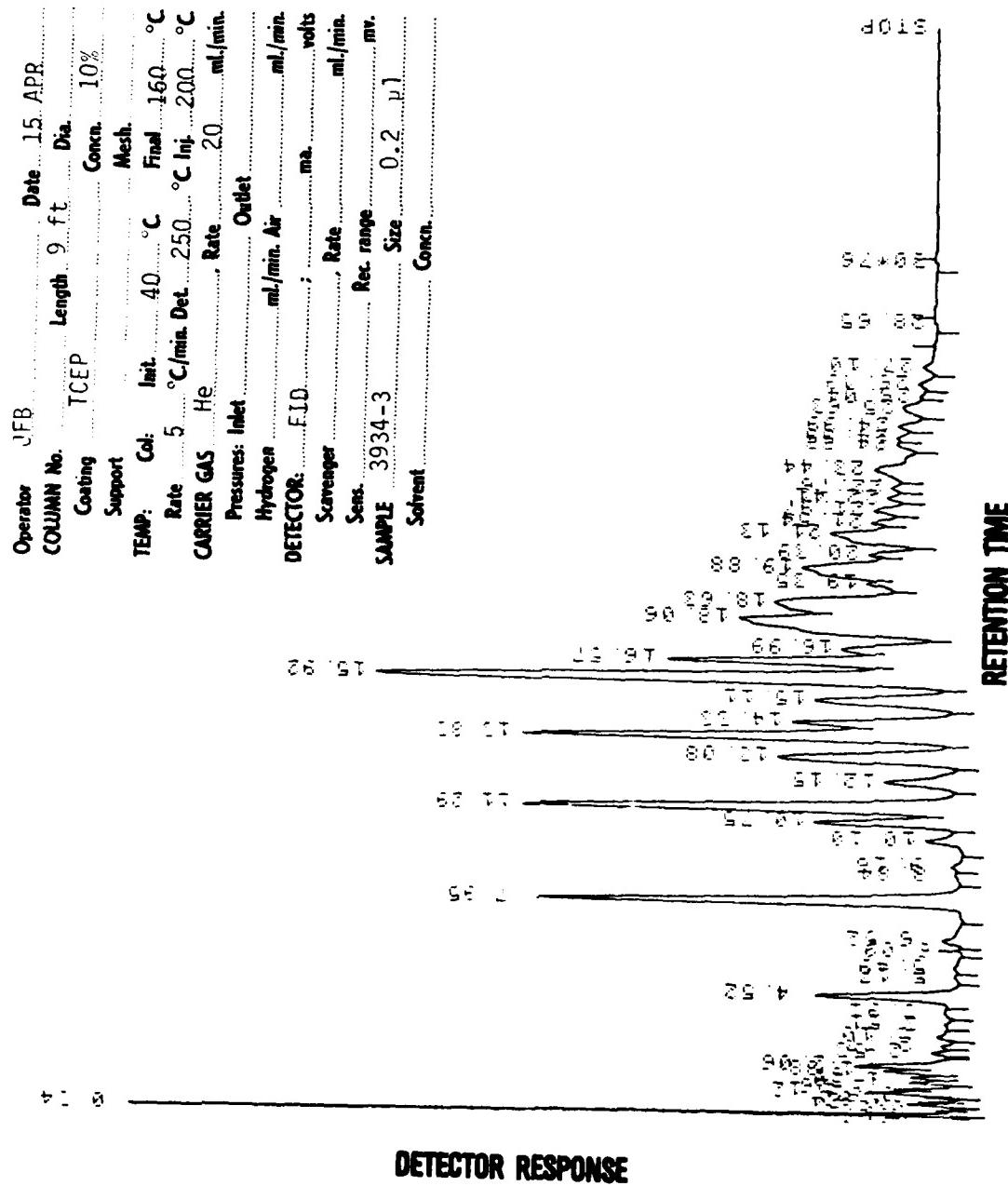


Figure 15. Gas Chromatogram of Sample 3934, LC Fraction 3

Operator	JFB	Date	16 APR
COLUMN No.	TCEP	Length	9 ft
Coating		Dia.	10%
Support		Concn.	
TEMP:	Col: Init. 40 °C	Mesh.	
	Rate 5 °C/min. Det. 250 °C	Final	160 °C
CARRIER GAS	He	Init.	200 °C
	Rate 20 ml/min.		
Pressures: Inlet		Outlet	
Hydrogen	ml/min. Air	ml/min.	
DETECTOR:	FID	mA.	
Scavenger		Rate	volts
Sens.		ml/min.	
SAMPLE	3934.4	Rec. range	mv.
Solvent		Size	0.2 μl.
		Concn.	

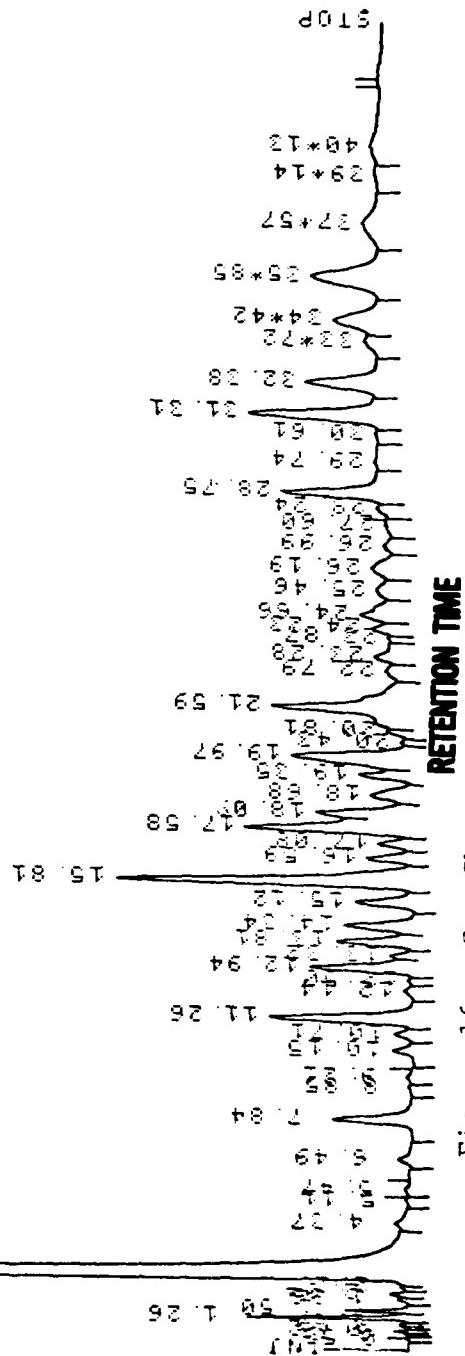


Figure 16. Gas Chromatogram of Sample 3934, LC Fraction 4

DETECTOR RESPONSE

Operator JFB Date 7 APR.
 COLUMN No. TCEP Length 9 ft. Dia. Concn. 10%
 Coating Support Mesh
 TEMP: Init. 40 °C Final 160 °C
 Rate 5 °C/min. Det. 250 °C Inf. 200 °C
 CARRIER GAS He Rate 20 ml./min.
 Pressures: Inlet Outlet
 Hydrogen ml./min. Air ml./min.
 DETECTOR FID. ; m.a. ml./min. volts
 Scavenger Rate ml./min.
 Sens. 3935-0 Rec. range m.v.
 SAMPLE Size 0.2 μ l
 Solvent Conc.

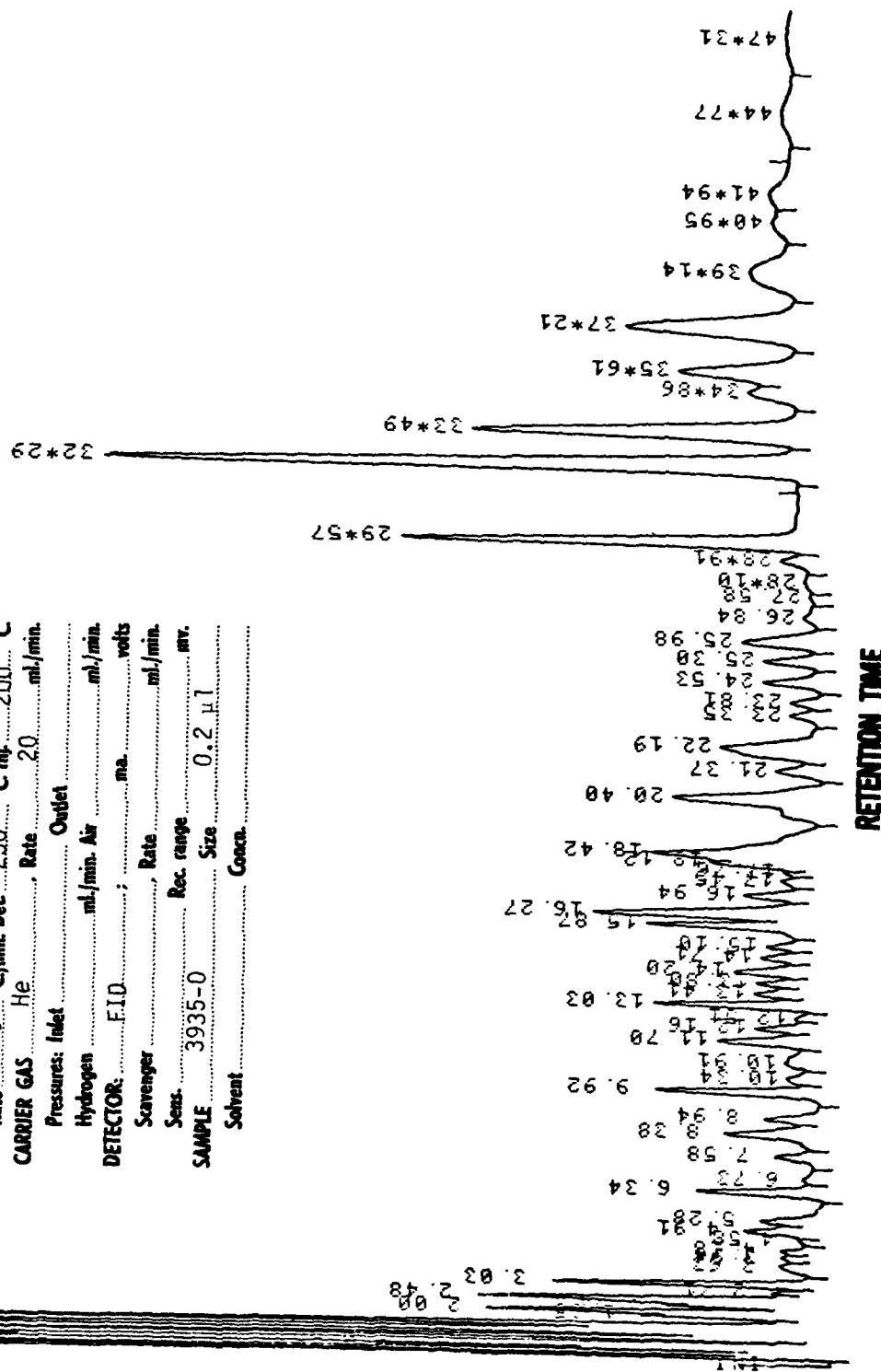


Figure 17. Gas Chromatogram of Sample 3935, Neat

Operator JFB Date 17 APR
 COLUMN No. TCEP Length 9 ft.
 Coating Concn. 10%
 Support Mesh.
 TEMP: Col. Init. 40 °C Final 160 °C
 Rate 5 °C/min. Det. 250 °C Inj. 200 °C
 CARRIER GAS He Rate 20 ml/min.
 Pressures: Inlet Outlet
 Hydrogen ml/min. Air ml/min.
 DETECTOR: FID ; m.a. volts
 Scavenger Rate ml/min.
 Sens. Rec. range mv.
 SAMPLE 3935-1 Size 0.2 μl
 Solvent Concn.

Figure 18. Gas Chromatogram of Sample 3935, LC Fraction 1

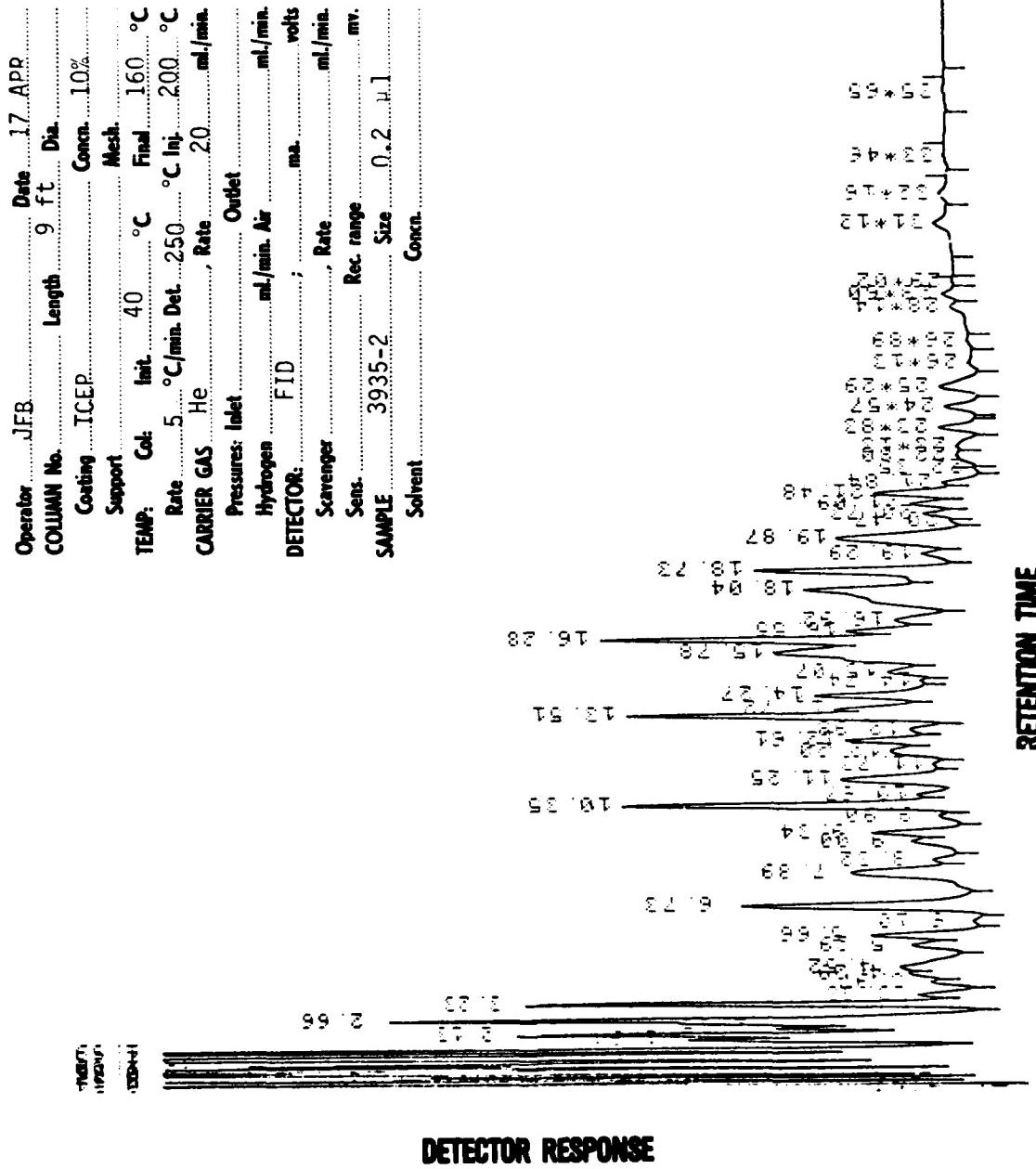


Figure 19. Gas Chromatogram of Sample 3935, LC Fraction 2

Operator JFB
 COLUMN No. TCEP Date 17 APR
 Coating Length 9 ft Dia. 10%
 Support Mesh Concn. 10%
 TEMP: Col. Init. 40 °C Final 160 °C
 Rate 5 °C/min. Det. 250 °C Init. 200 °C
 CARRIER GAS He Rate 20 ml/min.
 Pressures: Inlet Outlet Hydrogen ml/min. Air ml/min.
 DETECTOR: FID ma. Scavenger ma. Rate ml/min. volts
 Sens. 3935-3 Rec. range 2.0 μA
 SAMPLE Size 2.0 μL
 Solvent Concn.

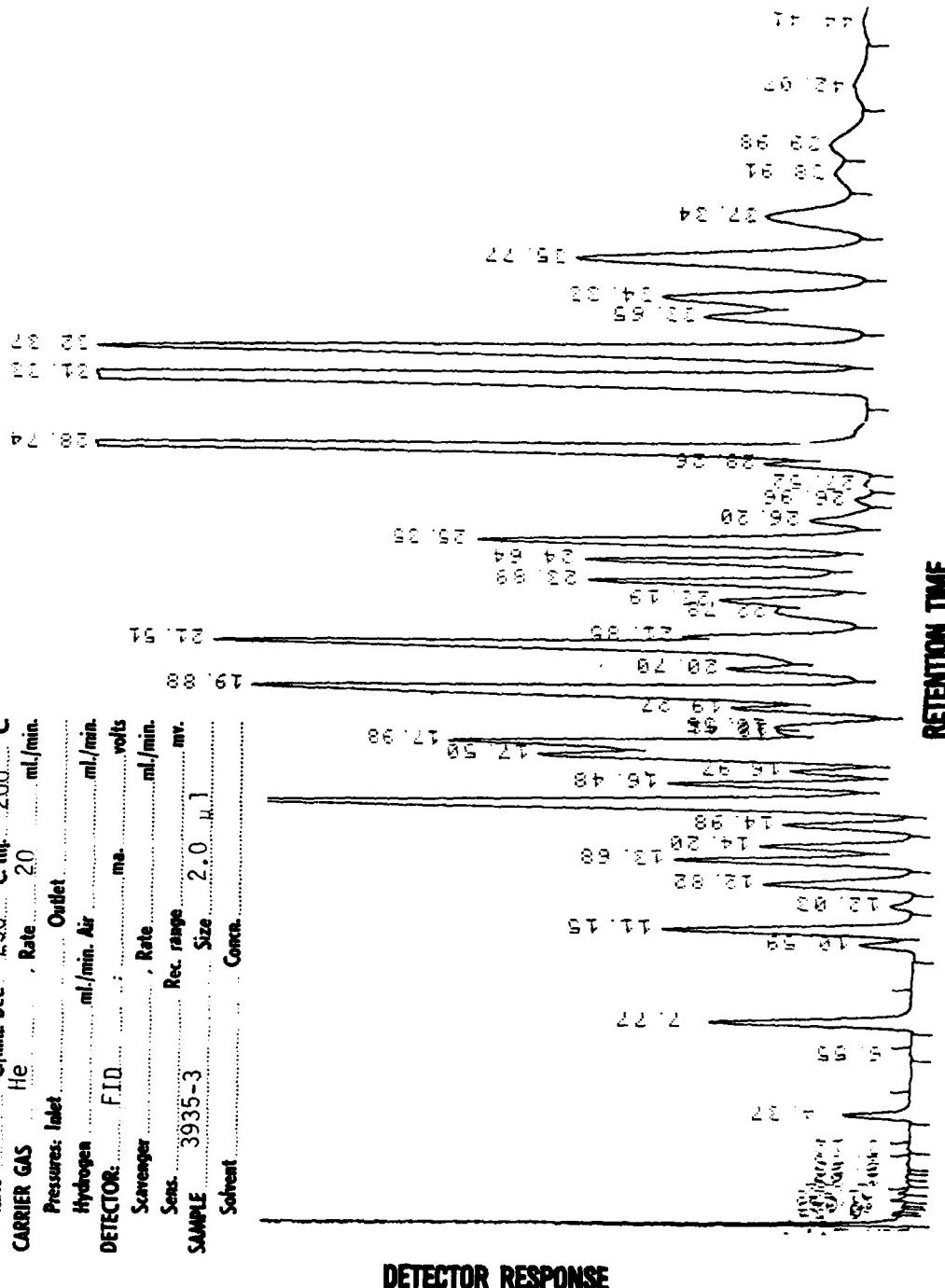


Figure 20. Gas Chromatogram of Sample 3935, LC Fraction 3

Operator	JFB	Date	16 APP.
COLUMN No.	TCEP	Length	9 ft
Coating		Dia.	
Support		Concn.	10%
TEMP.	Cal. Init. 40 °C	Final	160 °C
Rate	5 °C/min. Det. 250 °C	Inj.	200 °C
CARRIER GAS	He	Rate	20 ml./min.
Pressures: Inlet		Outlet	
Hydrogen	ml./min. Air	ml./min.	volts
DETECTOR:	FID	ma.	
Scavenger		Rate	ml./min.
Sens.	3935-4	Rec. range	mv.
SAMPLE	CH ₂ Cl ₂	Size	0.2 μl
Solvent		Concn.	

DETECTOR RESPONSE

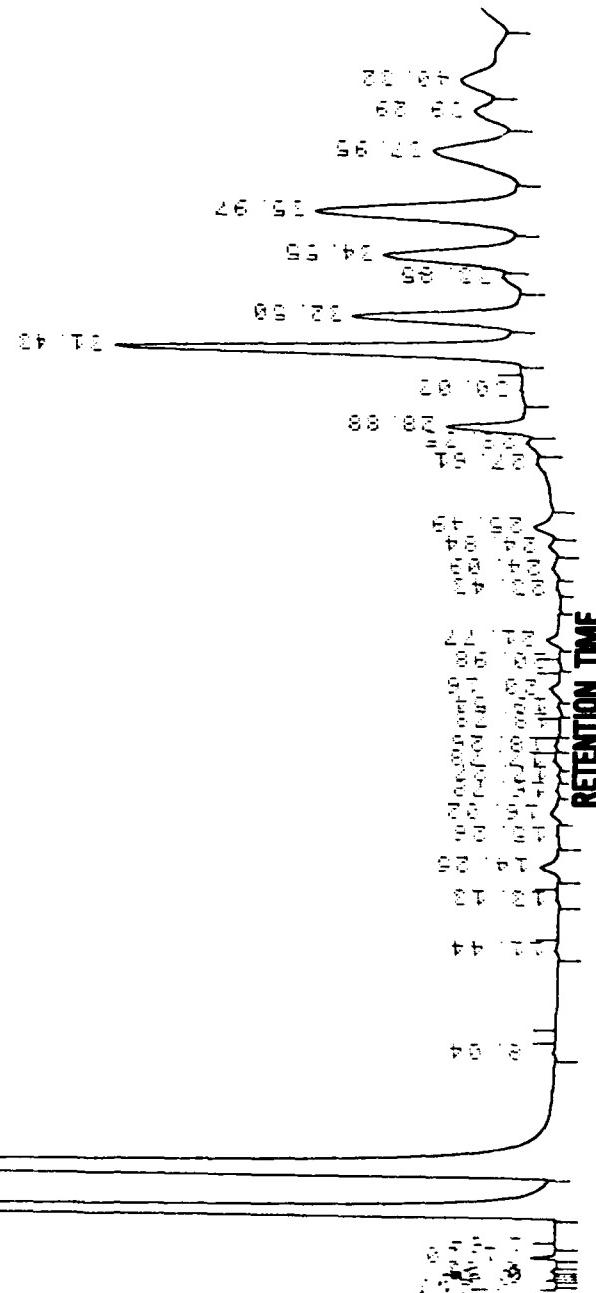


Figure 21. Gas Chromatogram of Sample 3935, LC Fraction

Operator	JFB	Date	18 APR
COLUMN No.	TCEP	Length	9 ft.
Coating		Dia.	10%
Support		Mesh	
TEMP:	Col: 5 °C/min. Det: 250 °C	Init. 40 °C	Final 160 °C
Rate	He	Rate	20 ml/min.
CARRIER GAS			
Pressures: Inlet		Outlet	
Hydrogen	ml/min.	Air	ml/min.
DETECTOR:	FID	;	ma.
Scavenger		Rate	ml/min.
Sens.		Rec. range	mv.
SAMPLE	3936-0	Size	0.3 uL
Solvent		Concn.	

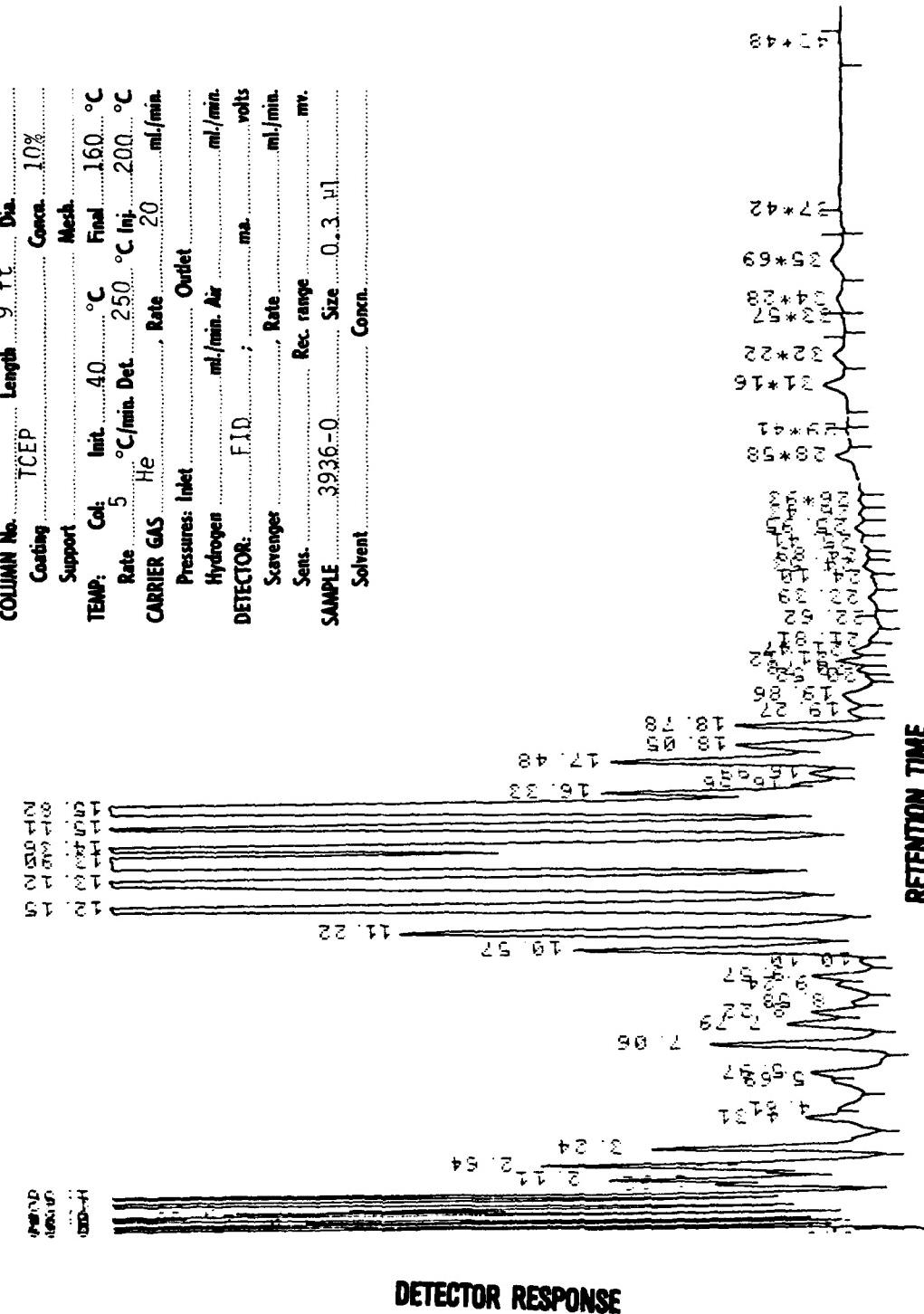


Figure 22. Gas Chromatogram of Sample 3936, Neat

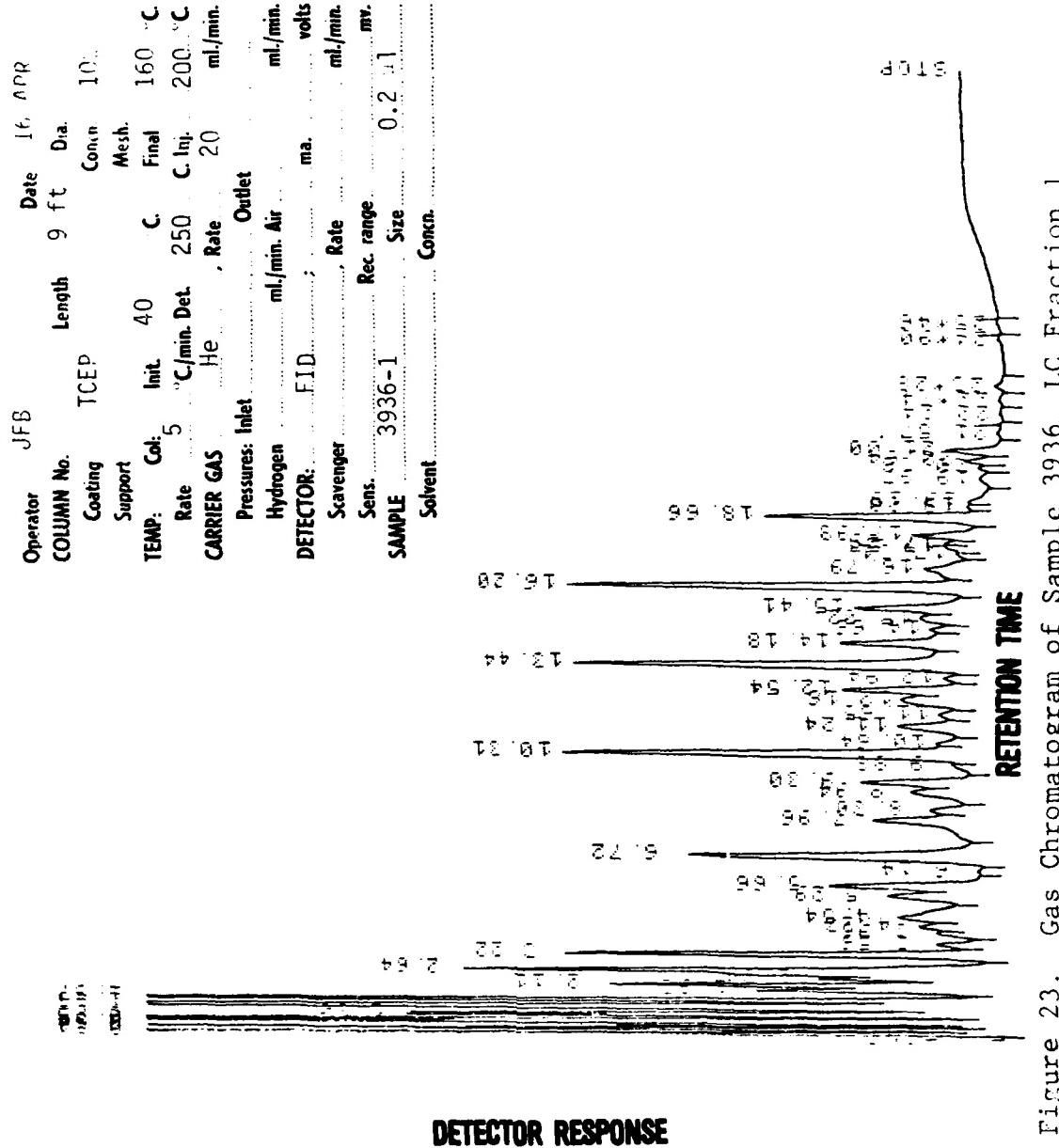


Figure 23. Gas Chromatogram of Sample 3936, LC Fraction 1

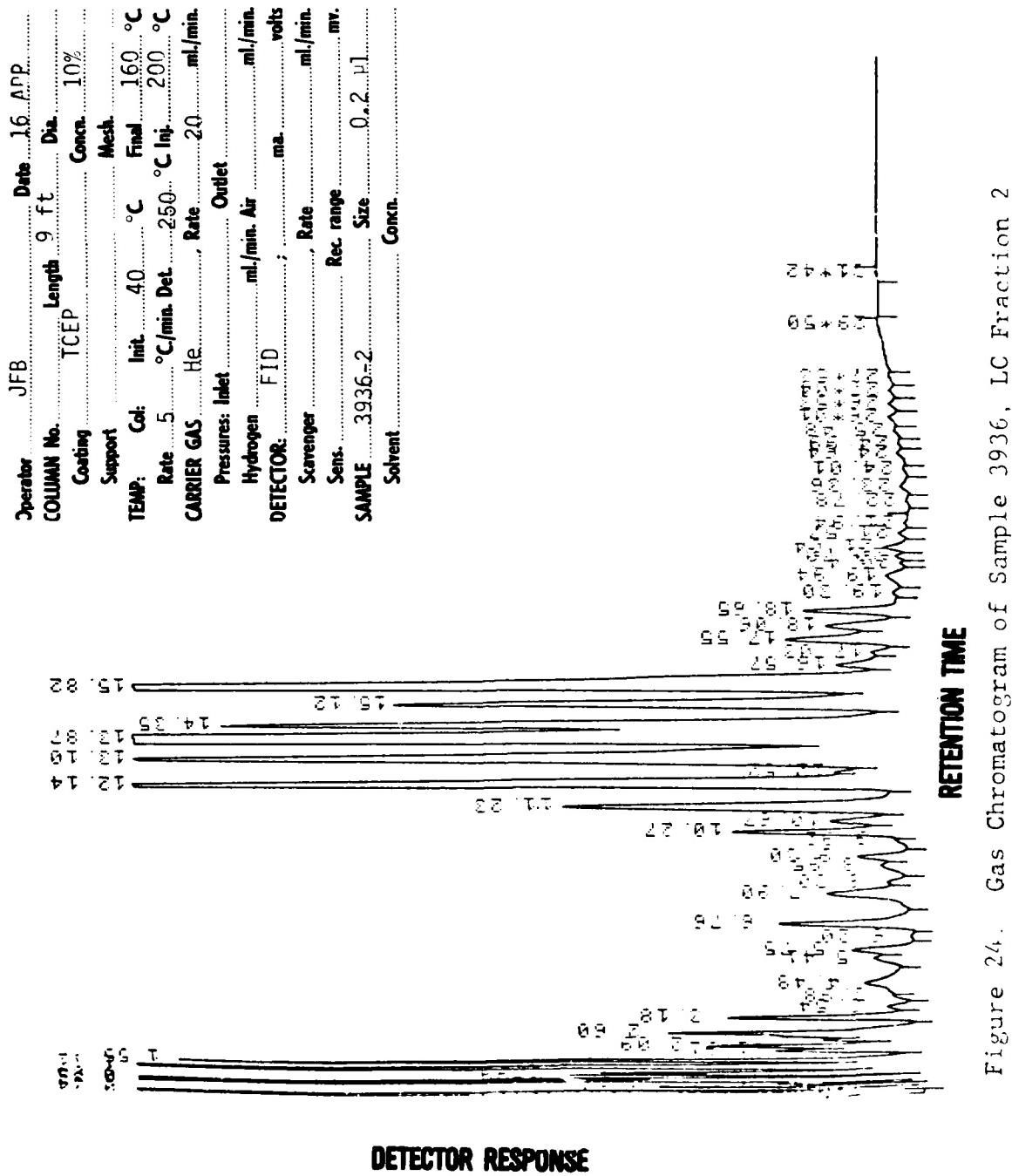


Figure 24. Gas Chromatogram of Sample 3936, LC Fraction 2

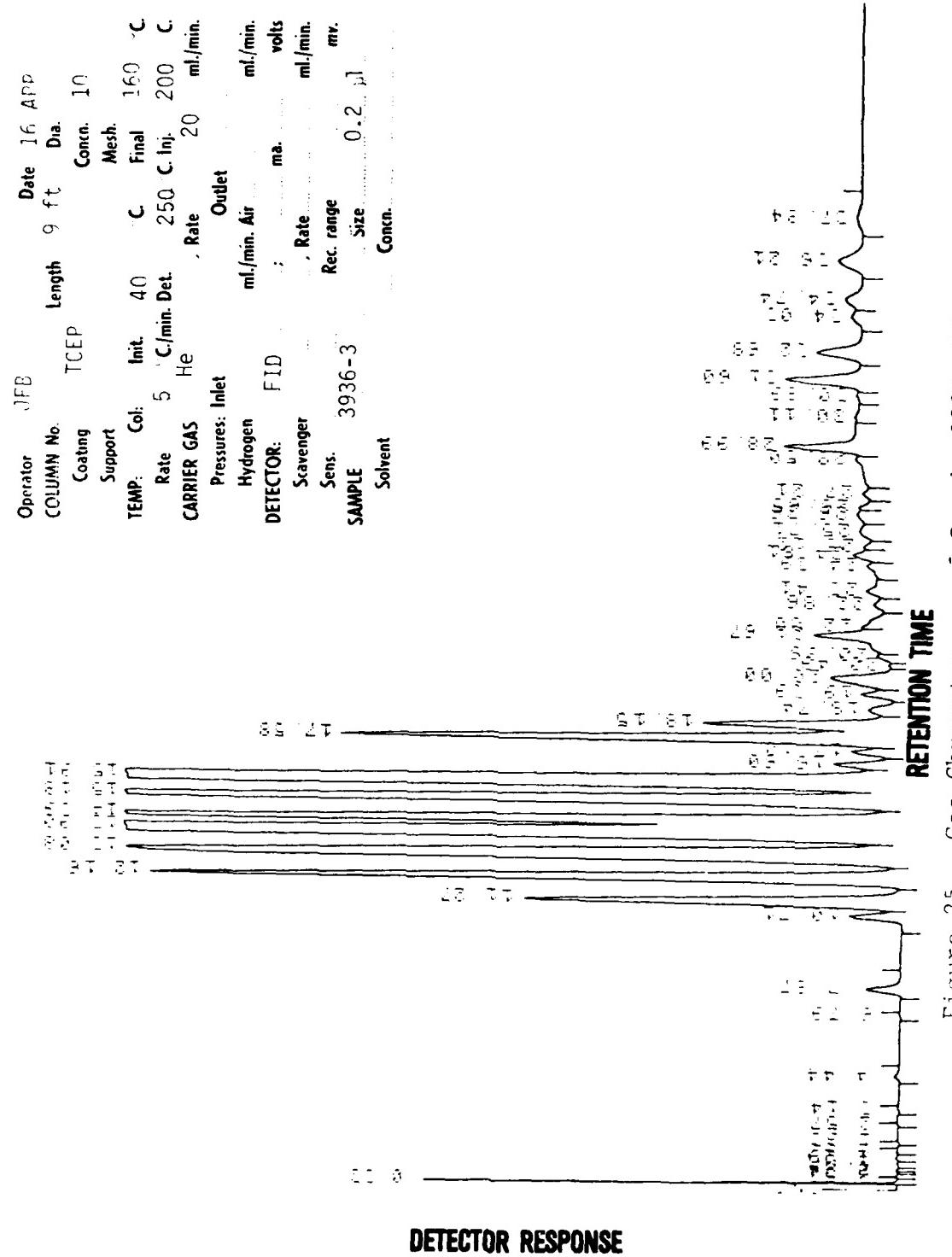


Figure 25. Gas Chromatogram of Sample 3936, LC Fraction 3

Operator	JFB	Date	16 APP
COLUMN No.		Length	9 ft
Coating	TCEP	Dia.	
Support		Mesh.	10%
TEMP:	Col: 5 °C/min. Det: 250 °C	Init.	40 °C
	He	Final	160 °C
CARRIER GAS		Inj.	200 °C
Pressures: Inlet		Rate	20 ml./min.
Hydrogen		Oudet	
DETECTOR:	FID	ml./min. Air	ml./min.
Scavenger		ma.	volts
Sens.		Rate	ml./min.
SAMPLE	3936-4	Rec. range	mv.
	CH ₂ Cl ₂	Size	0.2 μl.
Solvent		Concn.	

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DETECTOR RESPONSE



Figure 36. Gas Chromatogram of Sample 3936, LC Fraction 4

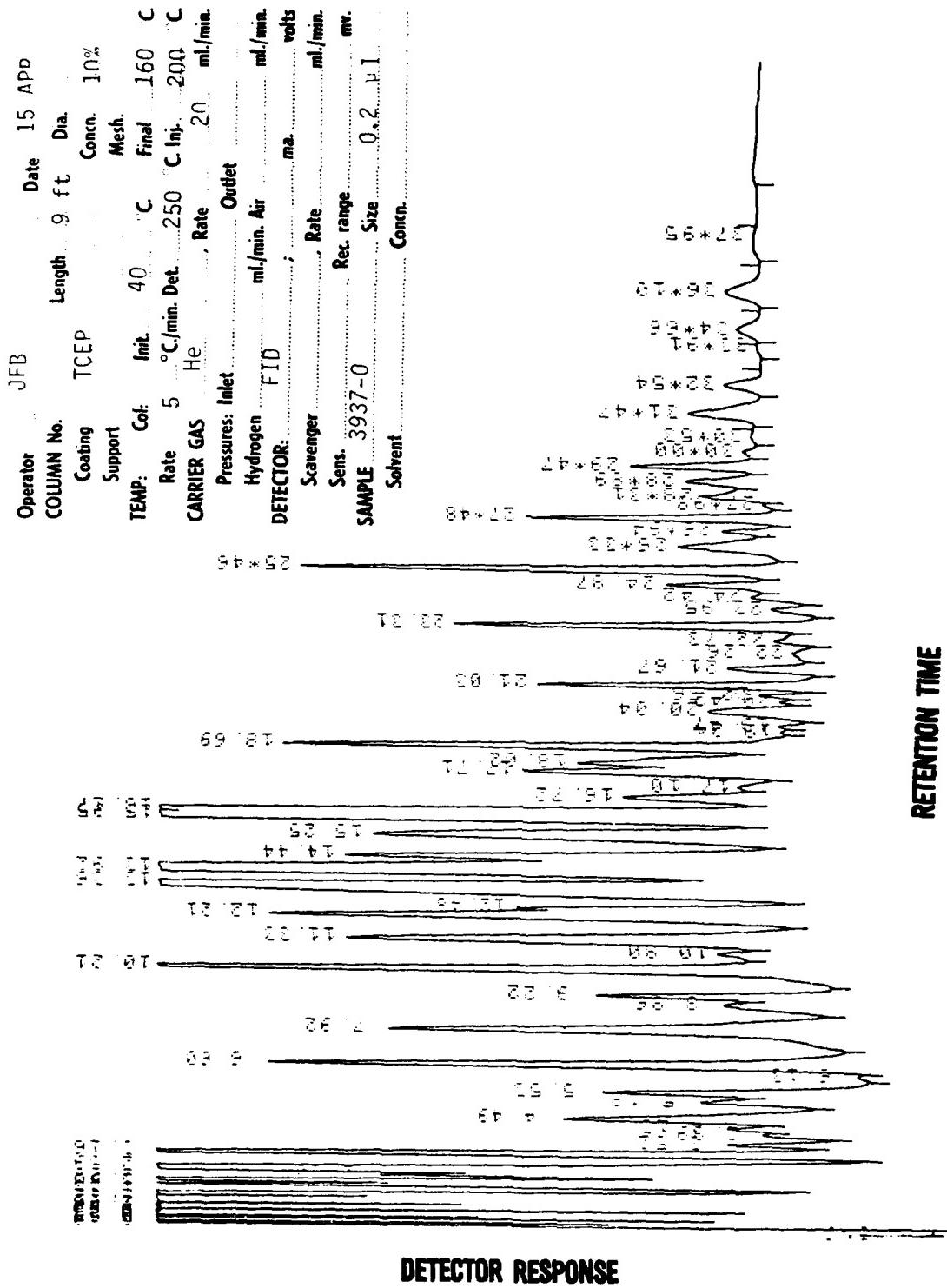


Figure 27. Gas Chromatogram of Sample 3937, Neat

Operator JFB Date 18 APR
 COLUMN No. TCEP Length 9 ft. Dia. 10%
 Coating
 Support Mesh. 160 °C
 Concn. 10%
 TEMP: Col. Init. 40 °C Final 160 °C
 Rate 5 °C/min. Det. 250 °C Ini. 200 °C
 CARRIER GAS He Rate 20 ml./min.
 Pressures: Inlet Outlet ml./min.
 Hydrogen ml./min. Air ml./min.
 DETECTOR: FID ma. Volts
 Scavenger Rate ml./min.
 Sens. Rec. range mV.
 SAMPLE Size C. 3 μ l
 Solvent Concn.

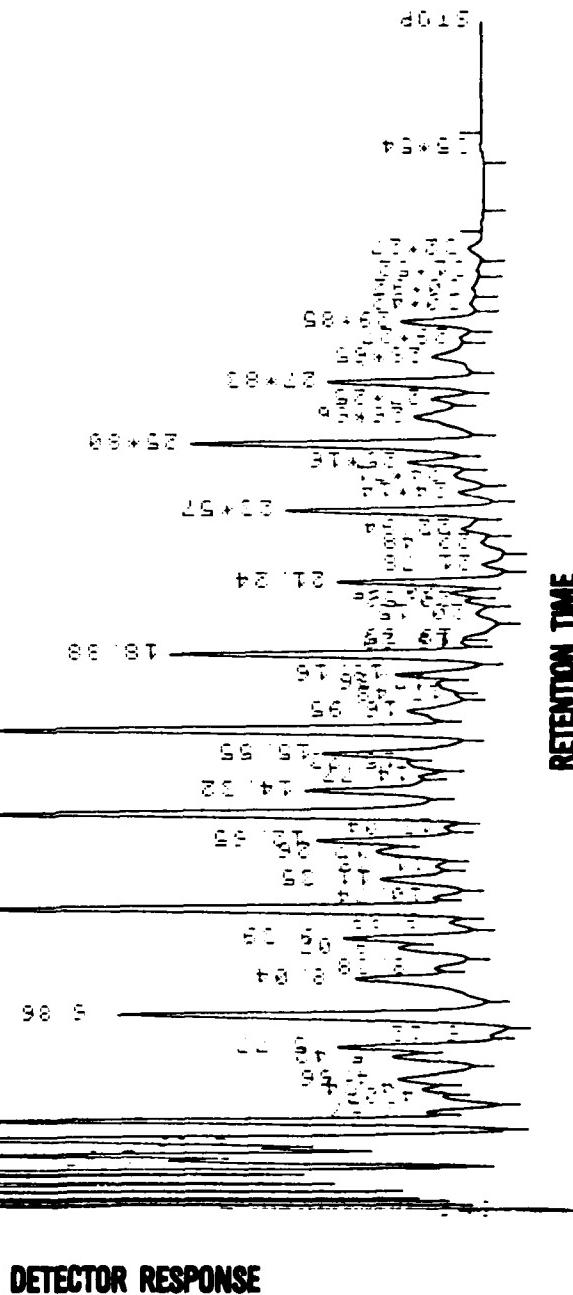
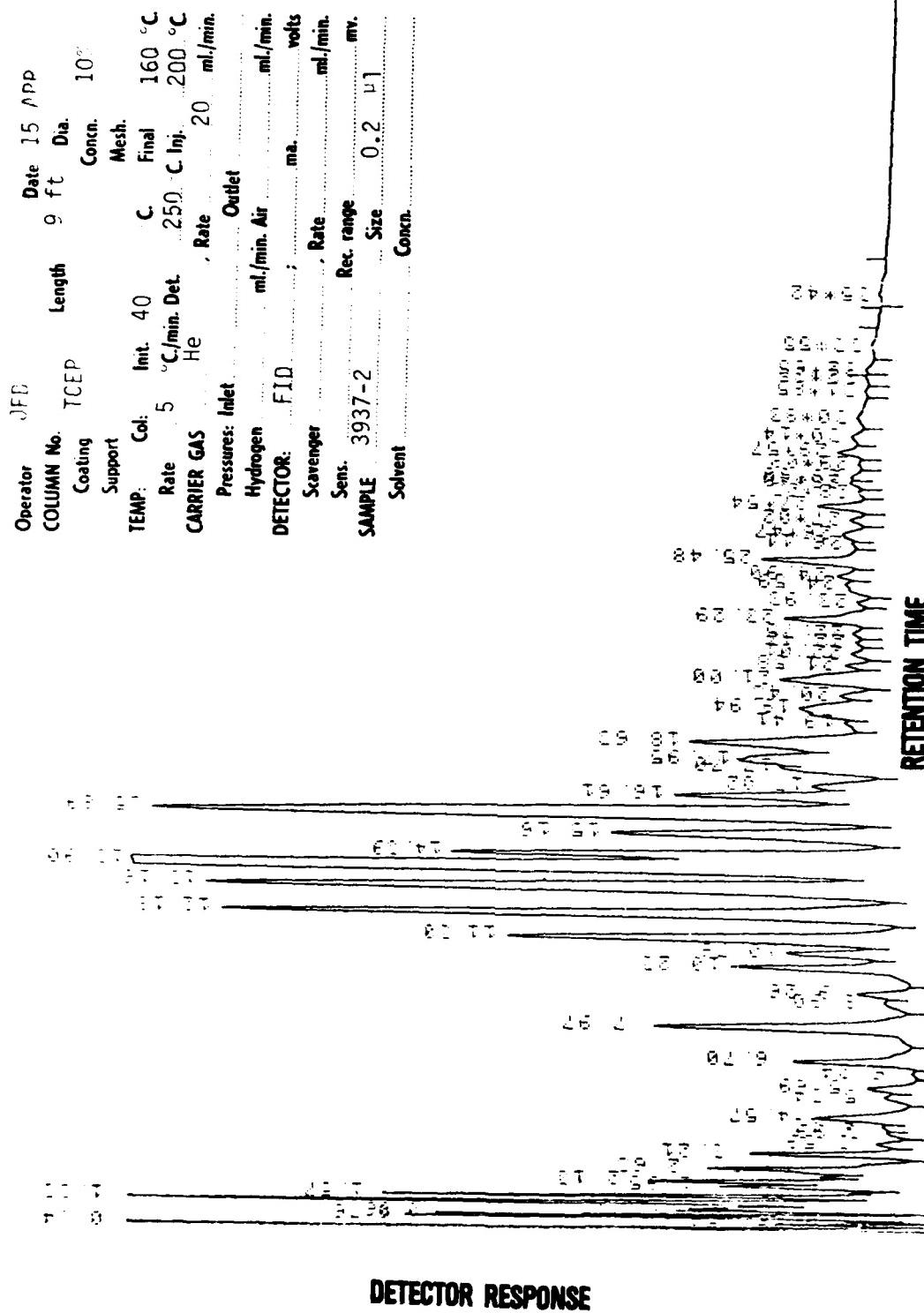
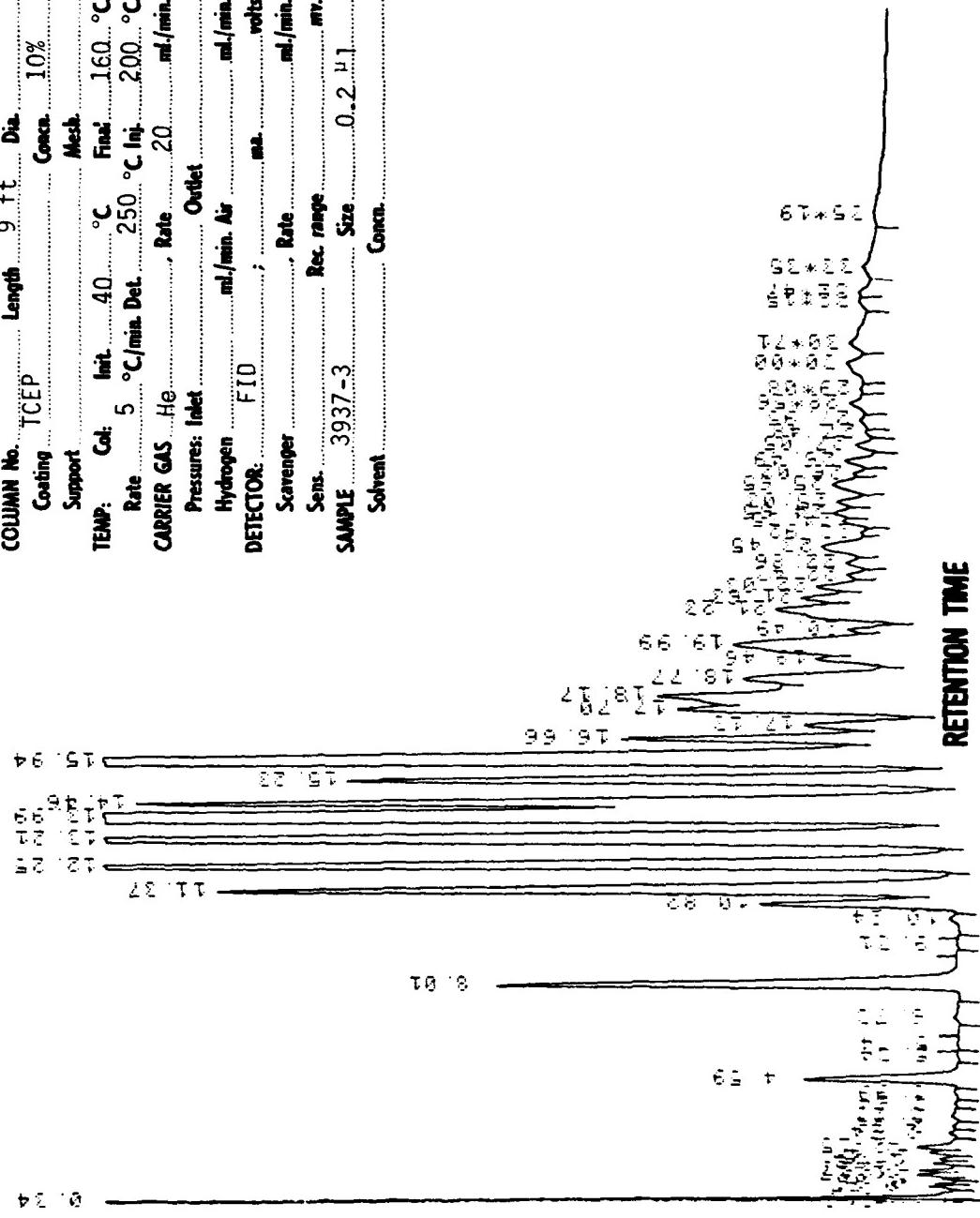


Figure 28. Gas Chromatogram of Sample 3937, LC Fraction 1



Operator	JFB	Date	15 APR
COLUMN No.	TCEP	Length	9 ft
Coating		Dia.	1/8 in.
Support		Coat.	10%
		Mesh	
TEMP.	Init. 5 °C/min Det. 250 °C	Final 160 °C	
Rate		Inj. 200 °C	
CARRIER GAS	He	Rate	20 ml/min.
Pressures: Inlet		Outlet	
Hydrogen	ml/min. Air	ml/min.	ml/min.
DETECTOR:	FID		
Scavenger		Rate	volts
Sens.	3937-3	Rec. range	ml/min.
SAMPLE		Size	0.2 μl
Solvent		Concn.	



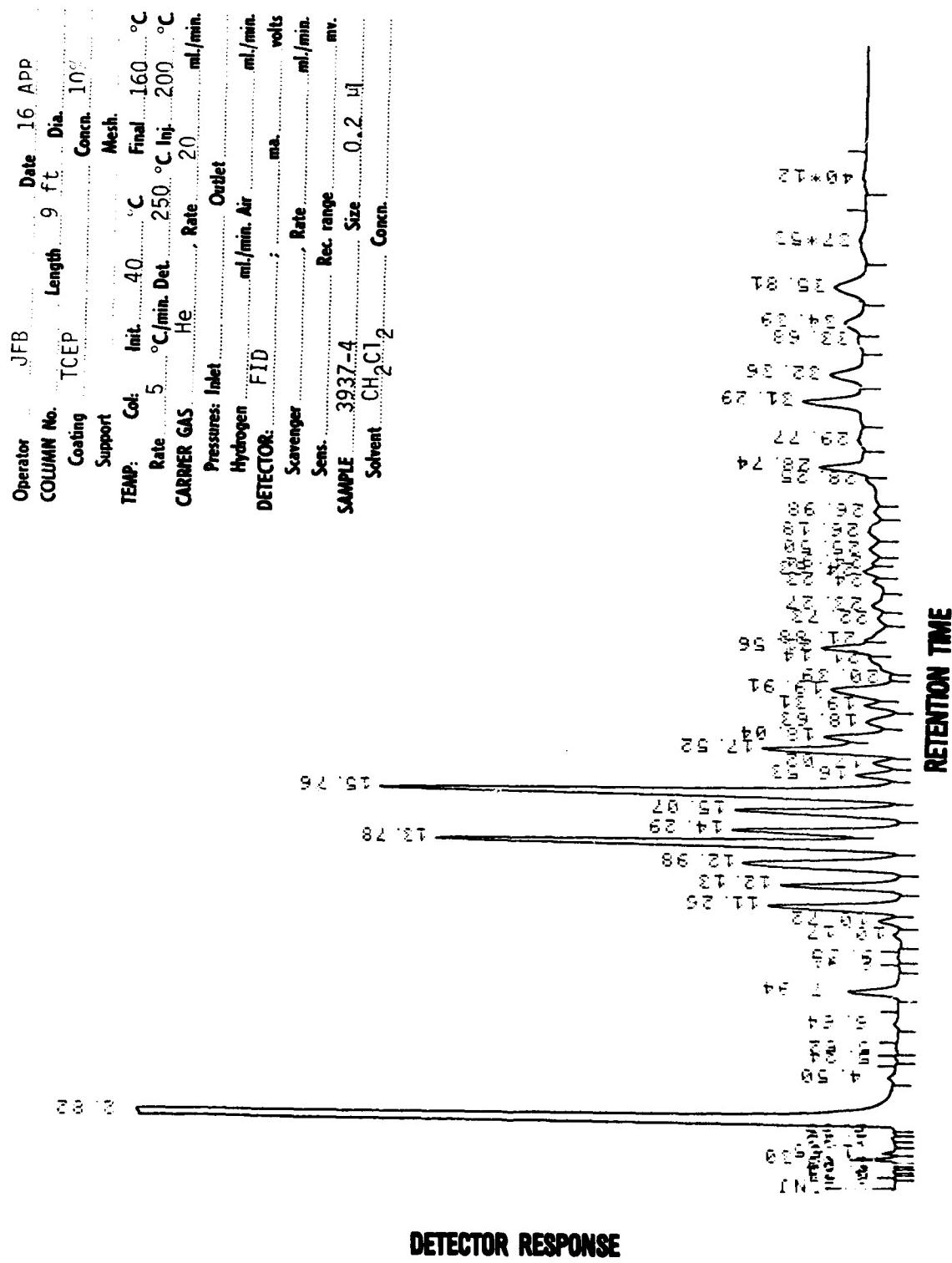


Figure 31. Gas Chromatogram of Sample 3937, LC Fraction 4

Operator	JFB	Column No.		Date	11. APP
Coating	TCEP	Length	9 ft	Conc.	10%
Support		Mesh			
TEMP:	Col: Init. 5 °C/min. Det. 250 °C, Int. 200 °C	Final	160 °C		
Rate	He	Rate	20 ml./min.		
CARRIER GAS					
Pressures: Inlet		Outlet			
Hydrogen	ml./min. Air	ml./min.			
DETECTOR: FID	FID	ma.	volts		
Scavenger		Rate	ml./min.		
Sens.		Ret. range	mv.		
SAMPLE	3938-0	Size	0.2 μ l		
Solvent		Concn.			

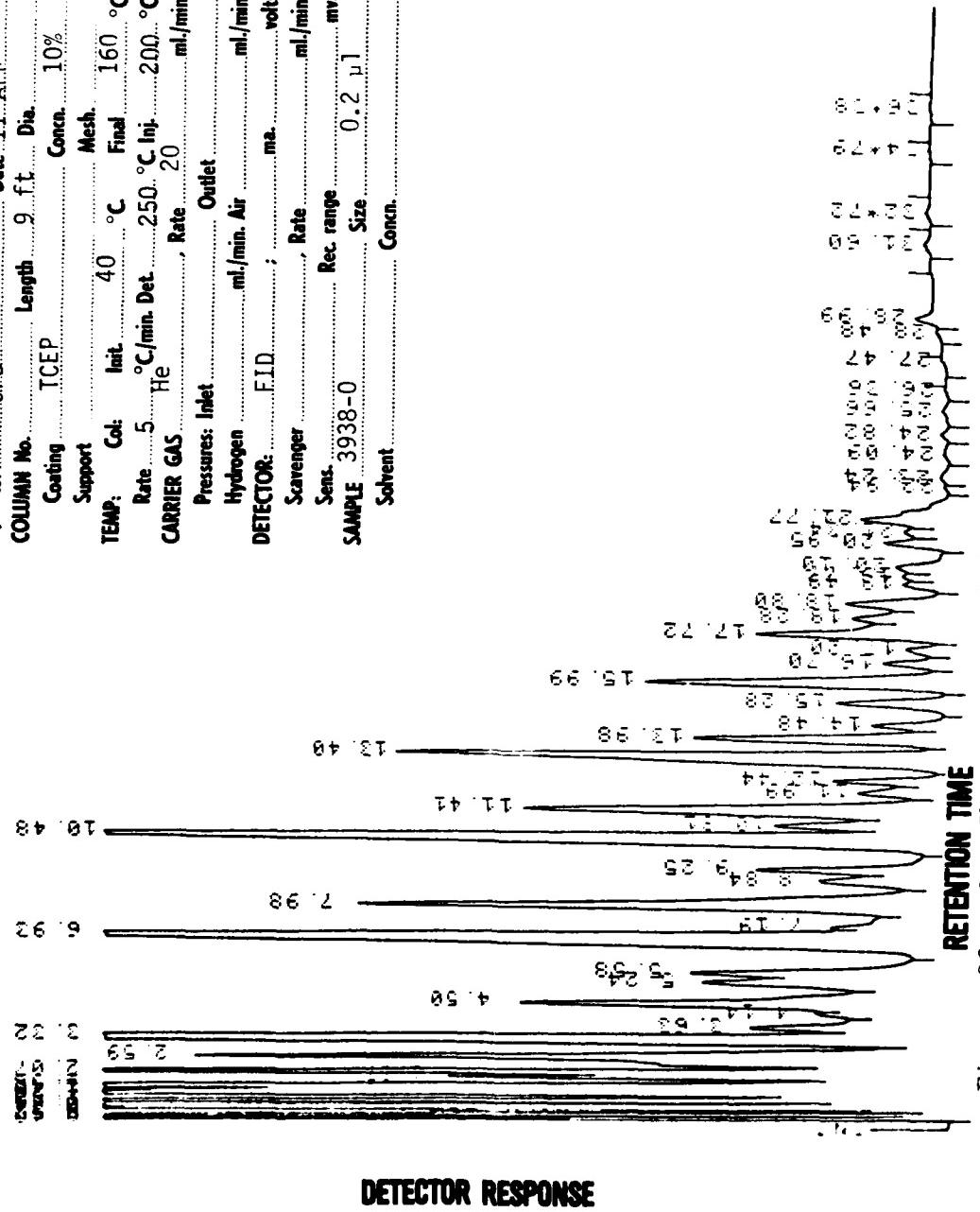


Figure 32. Gas Chromatogram of Sample 3938, Neat

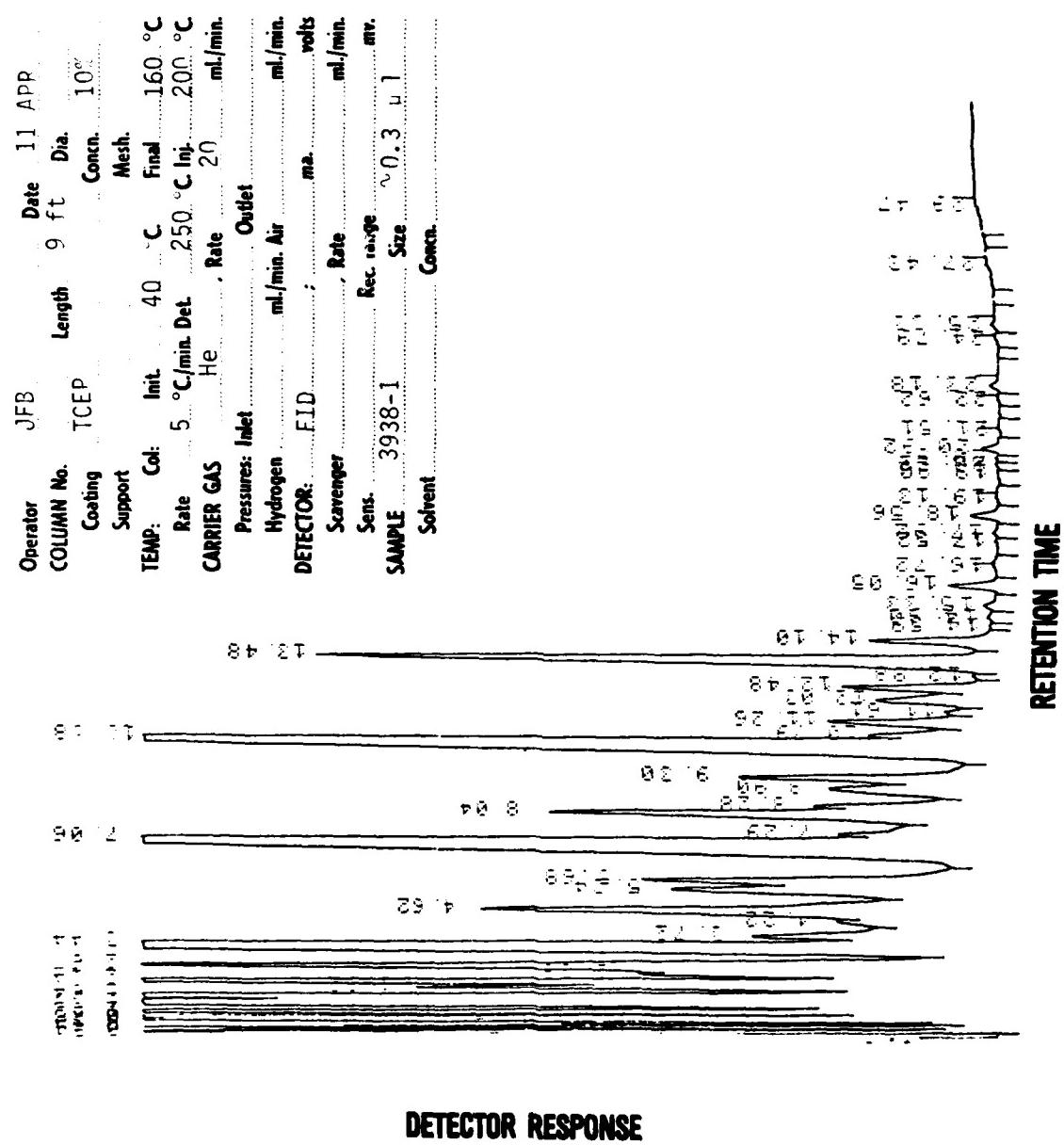


Figure 33. Gas Chromatogram of Sample 3938, LC Fraction 1

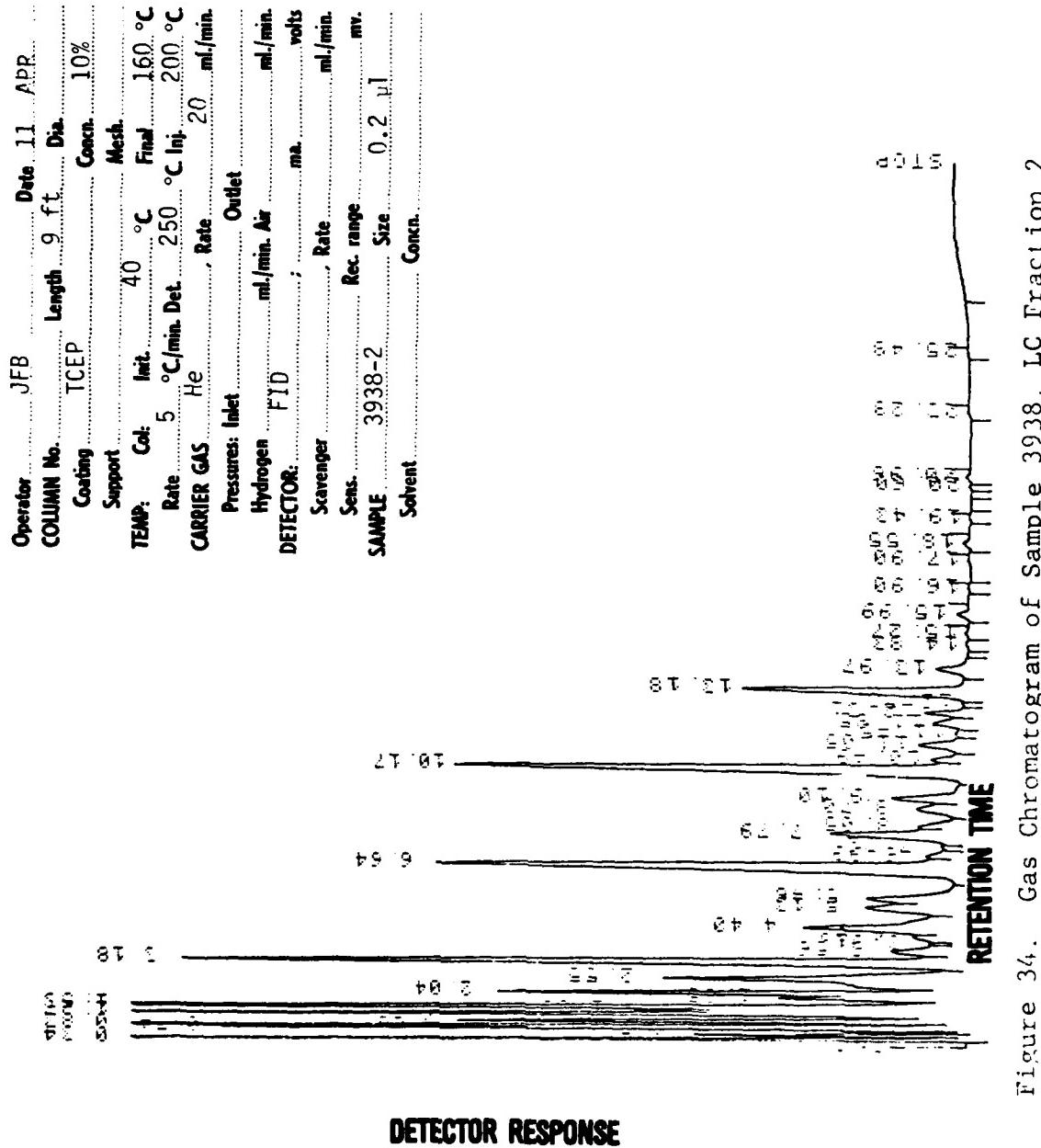
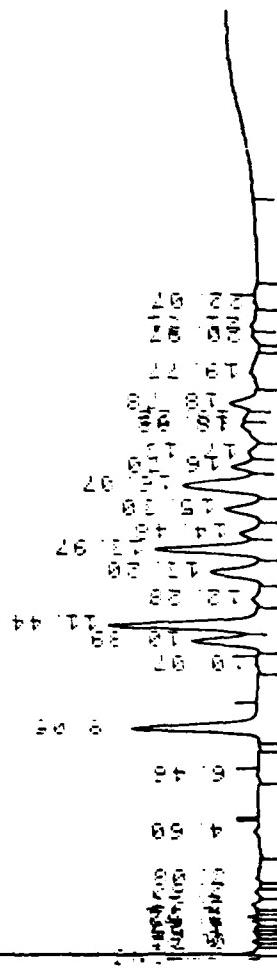


Figure 34. Gas Chromatogram of Sample 3938, LC Fraction 2

Operator JFB Date 11 APP
 COLUMN No. TCEP Length 9 ft Dia.
 Coating Conc. 10%
 Support Mesh.
 TEMP: Col. Init. 40 °C Final 160 °C
 Rate 5 °C/min. Det. 250 °C Inj. 200 °C
 CARRIER GAS He Rate 20 ml/min.
 Pressures: Inlet Outlet ml/min. ml/min.
 DETECTOR: FID ; ma. ma. volts
 Hydrogen ml/min. Air ml/min.
 Scavenger Rate ml/min.
 Seas. Rec. range mv.
 SAMPLE 3938-3 Size 0.2 uL
 Solvent Concn.



RETENTION TIME

Figure 35. Gas Chromatogram of Sample 3938, LC Fraction 3

Operator	JFB	Date	16 APR
COLUMN No.	TCEP	Length	9 ft.
Coating		Dia.	10%
Support		Concn.	
TEMP:	Cat: Init. 40 °C	Mesh.	
Rate	5 °C/min. Det. 250 °C min. He	Fin.	160 °C
CARRIER GAS	He	Rate	20 ml/min.
Pressures: Inlet	Outlet		
Hydrogen	ml/min. Air	ml/min.	
DETECTOR:	FID	ma.	volts
Scavenger		Rate	ml/min.
Sens.	3938-4	Rec. range	.mv.
SAMPLE	CH ₂ Cl ₂	Size	0.2 μ l
Solvent		Concn.	

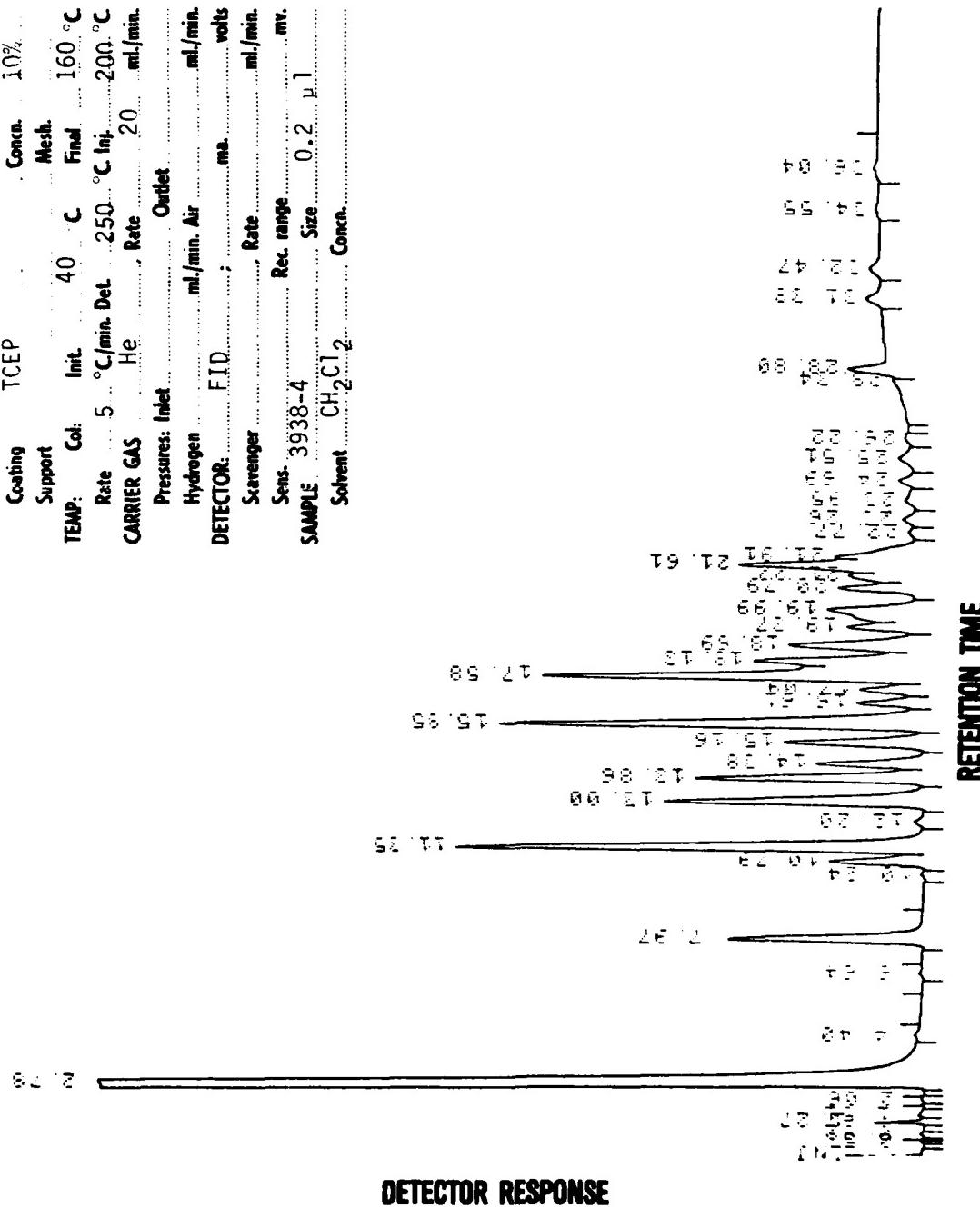


Figure 36. Gas Chromatogram of Sample 3938, LC Fraction 4

DETECTOR RESPONSE

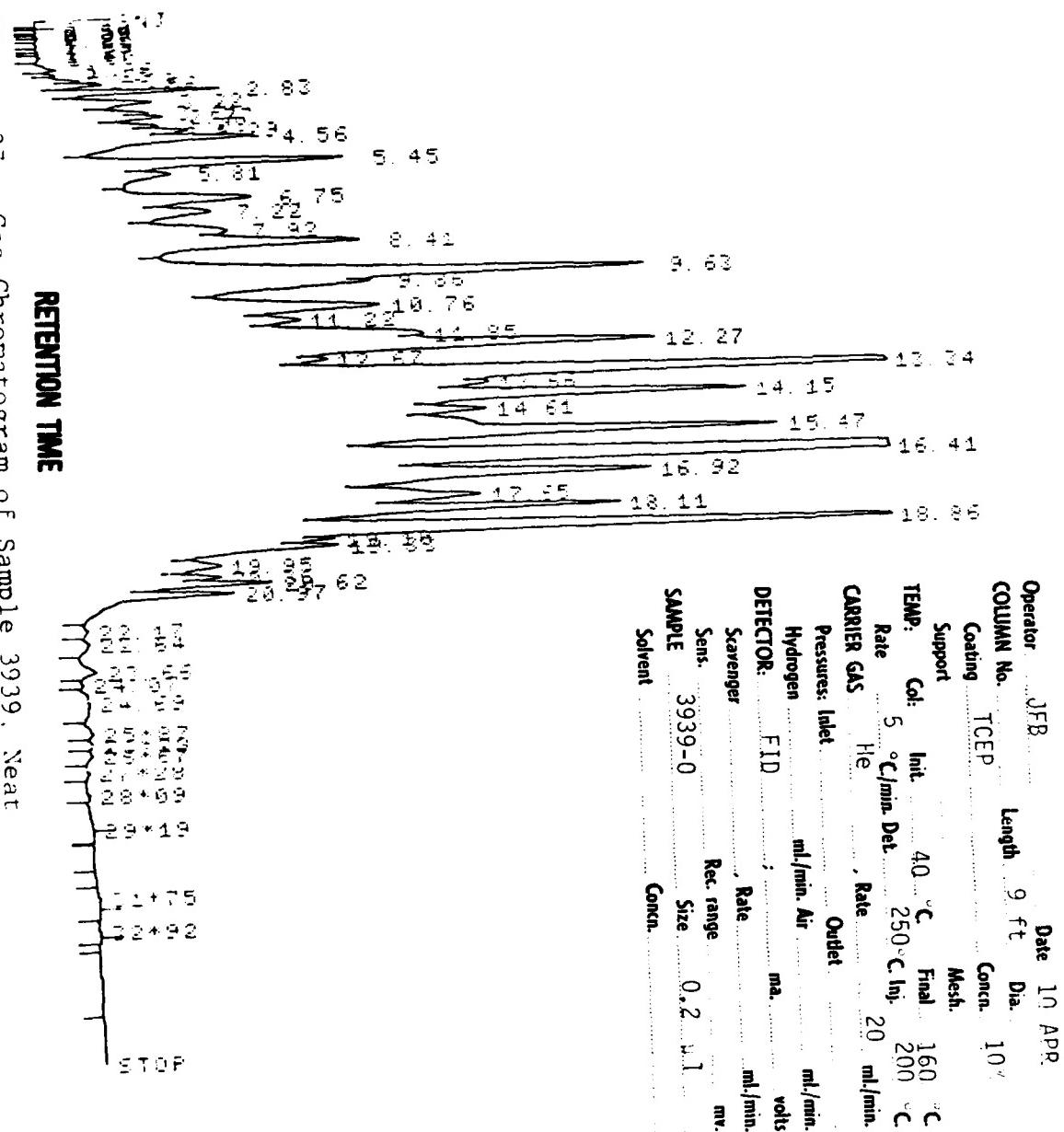


Figure 37. Gas Chromatogram of Sample 3939, Neat

Operator	JFB	Date	10 APR
COLUMN No.	TCEP	Length	9 ft
Coating		Dia.	10%
Support		Mesh	
TEMP:	Col: 5	Init. 40 °C	Final 160 °C
Rate	°C/min. Det. He	250 °C	Inj. 200 °C
CARRIER GAS		Rate 20 ml./min.	
Pressures: Inlet		Outlet	
Hydrogen		ml./min. Air	ml./min.
DETECTOR:	FID	ma.	volts
Scavenger		Rate	ml./min.
Sens.		Rec. range	mv.
SAMPLE	3939-1	Size	0.2 μl.
Solvent		Concn.	

DETECTOR RESPONSE

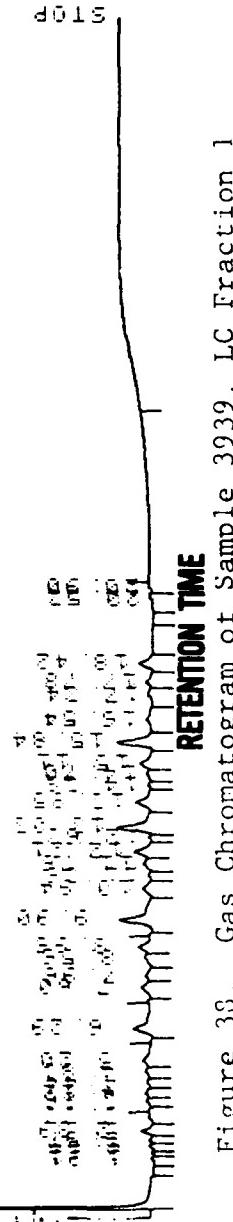


Figure 38. Gas Chromatogram of Sample 3939, LC Fraction 1

Operator	JFB	Date	10 APP
COLUMN No.	TCEP	Length	9 ft
Coating		Dia.	10 ^{c.}
Support		Concn.	10 ^{c.}
TEMP:	Col: Init. 40 °C	Final 160 °C	
Rate	5 °C/min. Det. 250 °C	Inj. 200 °C	
CARRIER GAS	He	Rate	20 ml./min.
Pressures: Inlet Outlet			
Hydrogen	ml./min. Air	ml./min.	ml./min.
DETECTOR:	FID	mA.	volts
Scavenger		Rate	ml./min.
Sens.	3939-2	Ret. range	mv.
SAMPLE		Size	~ 0.1 μ l
Solvent		Concn.	

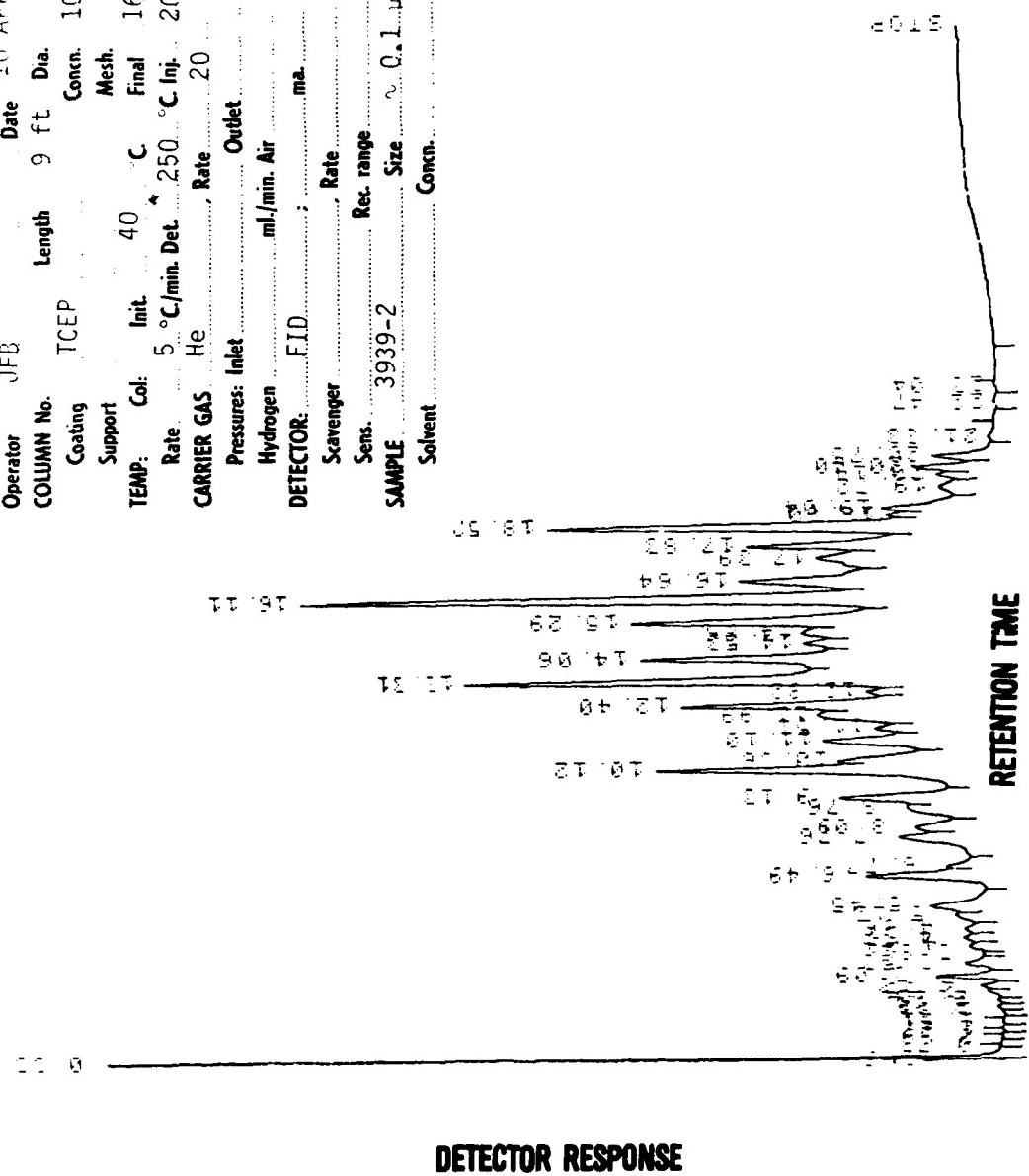
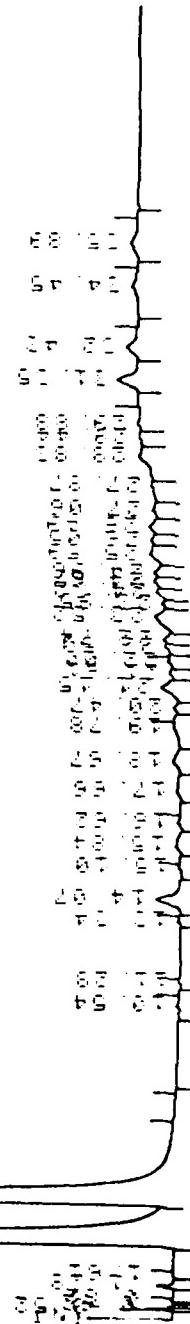


Figure 39. Gas Chromatogram of Sample 3939, LC Fraction 2

Operator	JFB	Length	9 ft.	Date	16 APR
COLUMN No.		Dia.		Concn.	10%
Coating	TCEP	Mesh			
Support					
TEMP. Col.	Init. 40 °C	Final 160 °C			
Rate	5 °C/min. Det. 250 °C	Inj. 200 °C			
CARRIER GAS	He	Rate	20 ml./min.		
Pressures: Inlet		Outlet			
Hydrogen	ml./min. Air	ml./min.			
DETECTOR:	FID	; Rate	mA.	volts	
Scavenger			mA.		
Sens.		Rec. range	ml./min.		
SAMPLE	3939-4	Size	0.2 uL		
Solvent	CH ₂ Cl ₂	Concn.			

4.15
2.82



DETECTOR RESPONSE

Figure 40. Gas Chromatogram of Sample 3939, LC Fraction 4

SECTION IV
CONCLUSIONS AND RECOMMENDATIONS

The accumulated data from the separation and analysis of the various fuel samples, as well as the model compounds, indicate that the method developed is feasible for the intended purpose. Good separations were achieved for aliphatic and aromatic compounds. Fairly good separation of olefinic compounds was also realized. However, relatively poor or no separation occurred between linear, branched, and cyclic aliphatic compounds.

Experiments with the use of longer columns suggest that partial separation of the various aliphatic hydrocarbon classes might be at least feasible.

The results also indicate that the plate efficiencies of the silica gel columns used in this system were rather poor. This fact may have been partly due to channeling resulting from bubble formation in the low-boiling solvent. The use of a totally pressurized system with continuous monitoring of the eluate, rather than intermittent fraction collection, should alleviate this problem.

Isobutane was selected as the mobile phase because of its reasonable cost, its low boiling point, and its generally innocuous nature. This compound was found, in fact, to be easily separable from the collected sample fractions. However, better resolution of compound classes might be achieved by using a low-boiling perfluorinated solvent. Compounds of this type are generally less polar than hydrocarbons, and should therefore provide better selectivity for the different aliphatic compound classes. Indeed, a dual solvent system employing both fluorocarbons and hydrocarbon mobile phases might be devised which could greatly enhance the separation of the fuel components.

In summary, we believe that the general objectives of this exploratory project were accomplished. Although the desired degree of separation was not obtained for all the compound classes, further work along the lines suggested above should greatly improve the separation efficiency of the method.

SECTION V

ADDITIONAL CONSIDERATIONS

A. Environmental Impact

It is conceivable that the separation method, as devised, could help in the ultimate development of fuel formulations having better air pollution properties than existing fuels. The environmental impact of the experimental method itself, however, is negligible. In the event that other mobile phases, particularly any of the various fluorocarbons, were used as suggested previously in this report, measures would have to be taken to recover them rather than venting them to the atmosphere. Such recovery would also be desirable from an economic standpoint, since such compounds are relatively costly.

B. Suggestions For Method Scale-Up

The method as developed, using 10-mm ID columns, is applicable to samples up to a maximum of a few hundred microliters. In order to provide the capacity for sample volumes up to about 10 mL, the column diameter would have to be increased to about 50 mm. This larger column diameter would necessitate mobile phase flow rates up to 50 mL per minute in order to maintain the same solvent linear velocity, and therefore preserve the separation patterns observed in the present method. Such large flow rates would necessitate the use of relatively large quantities of mobile phase, and for safety purposes would no doubt require the design of some type of solvent recovery system.

The separation of even larger amounts of fuel, e. g., 100 mL, could be achieved using a 50-mm preparative column, and running repetitive injections of 10 mL samples. The fractions would then be combined from successive runs. This system would, of course, be rather tedious and would require good control of flow rates, temperature, and other chromatographic parameters.

Scale-up to liter quantities seems unfeasible using the system described in this report. In order to separate one liter of fuel in a single run, column diameters up to 130 cm would be necessary. Such columns are very difficult to pack and generally provide low efficiencies. Furthermore, the mobile phase flow rates and volumes required would be prohibitive. A better technique would probably involve fractional distillation of the fuels.